APPLICATION OF CHEMICAL ANALYSIS AS AN AID TO WASTE MINIMISATION IN THE ELECTROPLATING INDUSTRY

By

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ABSTRACT

A chromium plating line used by a local company was monitored to identify any potential waste minimisation opportunities. Plating of the workpiece surface is carried out by immersing the workpiece in seven process (treatment) solutions including nickel and chromium plating baths. Between each process step the workpieces are rinsed.

The chromium plating process was evaluated using the results of a waste minimisation audit. This involved gathering data on the composition, flow rates and costs of the inputs of the process. Two types of data were collected namely new and existing data. The new data included chemical monitoring (concentration levels of Ni, Cr, Na, S, B, P, Si, Fe, Cu, Zn, Pb as well as conductivity, TDS, SS and pH measurements) and water usage data. The existing data included raw materials, utility inputs, composition of process solutions and product outputs. The data were analysed using three established waste minimisation techniques. The Water Economy Assessment (a form of Monitoring and Targeting) results were determined using an empirically derived model. The Water Balance and True Cost of Waste results were obtained through more detailed calculations using the results of the chemical analysis.

The results from the audit showed that the water usage on the chromium plating line has the highest waste minimisation potential. The True Cost of Waste analysis showed there is no significant chemical wastage in the effluent stream. The potential savings of the effluent stream was negligible (approximately R10 for 238 days). Drag-out calculations were also performed and showed that the drag-out volumes were in good agreement with the typical volumes found in the metal finishing industry. Intervention using simple low-cost and no-cost waste minimisation opportunities were recommended as a first step before contemplating further focus areas for technical or feasibility studies.

DECLARATION

I hereby certify that this research is the result of my own investigation which has not already been accepted in substance for any degree and is not being submitted in candidature for any other degree.

Signed…….

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I hereby certify that this statement is correct.

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CONTENTS

List of Abbreviations

BD	Below detection limit
CCD	Charge Coupled Device
CID	Charge Injection Device
CPL	Chromium Plating Line
HDPE	High density polyethylene
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
MSDS	Material Safety Data Sheet
NM	Not Measured
OC	Operating Cycle
PDA	Photodiode array
PMT	Photomultiplier tube
PVC	Polyvinyl chloride
SP	Sample Period
SS	Suspended Solids
TDS	Total Dissolved Solids
WM	Umgeni Municipality Water Meter

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CHAPTER 1

DISSERTATION STRUCTURE

This dissertation begins with an introduction into the background behind the electroplating process employed by a manufacturing company in Howick, near Pietermaritzburg. A detailed description is given in Chapter 2 of the process involved in chromium plating. This looks at the pre-treatment and post-treatment steps as well as nickel and chromium plating. In particular it looks at the chemistry of the pre-treatment, the post-treatment, nickel and chromium plating solutions and how this effects different types of rinsing systems. It also describes the techniques and hardware in common use on the chromium plating lines.

A literature review on waste minimisation programmes is given in Chapter 3. This describes the waste audit procedure and the established waste minimisation options and opportunities in the electroplating industry. The four assessment techniques used in the waste audit section of the waste minimisation programme will be outlined in this chapter.

In Chapter 4, the scope and aims of this project are outlined. They are presented at this stage to enable the reader to be conversant with the terminology and concepts used in the electroplating plating process being monitored.

Chapter 5 gives a detailed description of the host company for this project. This includes general information on the structure of the company and specific details on the electroplating process. General information includes data on the products manufactured, equipment used in the manufacturing, working hours and on-site facilities. Specific details are reported on the manufacture of these products and the techniques and chemicals used in their coating.

The last four chapters all deal with the research methodology used in and findings obtained from the project. Chapter 6 describes the methods used in the investigation of the process. This includes laboratory elemental chemical analysis and suspended solids and total dissolved solids analysis and measurements made with direct reading instruments. Data were also collected from company records and municipality water bills. The results of these activities are presented in Chapter 7. These results are discussed in Chapter 8 and conclusions and recommendations are presented in Chapter 9.

CHAPTER 2

INTRODUCTION TO THE ELECTROPLATING PROCESS

Electroplating is essentially the coating of an object with a thin layer of metal by use of electricity.[1,2] Electrodeposited metals are used to provide a thin surface coating which has some property or properties superior to that of the substrate onto which it is deposited.[3,4,5] The most popular metals used for electroplating are gold, silver, chromium, cadmium, copper, nickel, tin and zinc.[1]

There are three main reasons for electroplating:
(1) To improve the appearance,
(2) To slow or prevent corrosion (rust) and
(3) To increase the strength and resistance to wear.
An article may be electroplated for any or all three of the above reasons.[1,2,4,5,6]

Electroplating is used to enhance the properties of many different objects including hardware, jewellery, automobiles, appliances, heavy equipment and door and window fittings.[1,6]

2.1 Breakdown of the Electroplating Process

There are three processing stages a workpiece undergoes when being electroplated. Each stage involves moving the workpiece through a series of baths or tanks containing certain chemicals designed to complete certain steps in the process. The tanks containing the chemicals required for the surface treatment are referred to as process tanks. The three stages are: surface preparation (pre-treatment); surface treatment and post-treatment.[2,6] Each stage is followed by the adequate rinsing of the workpiece (see Figure 2.1).

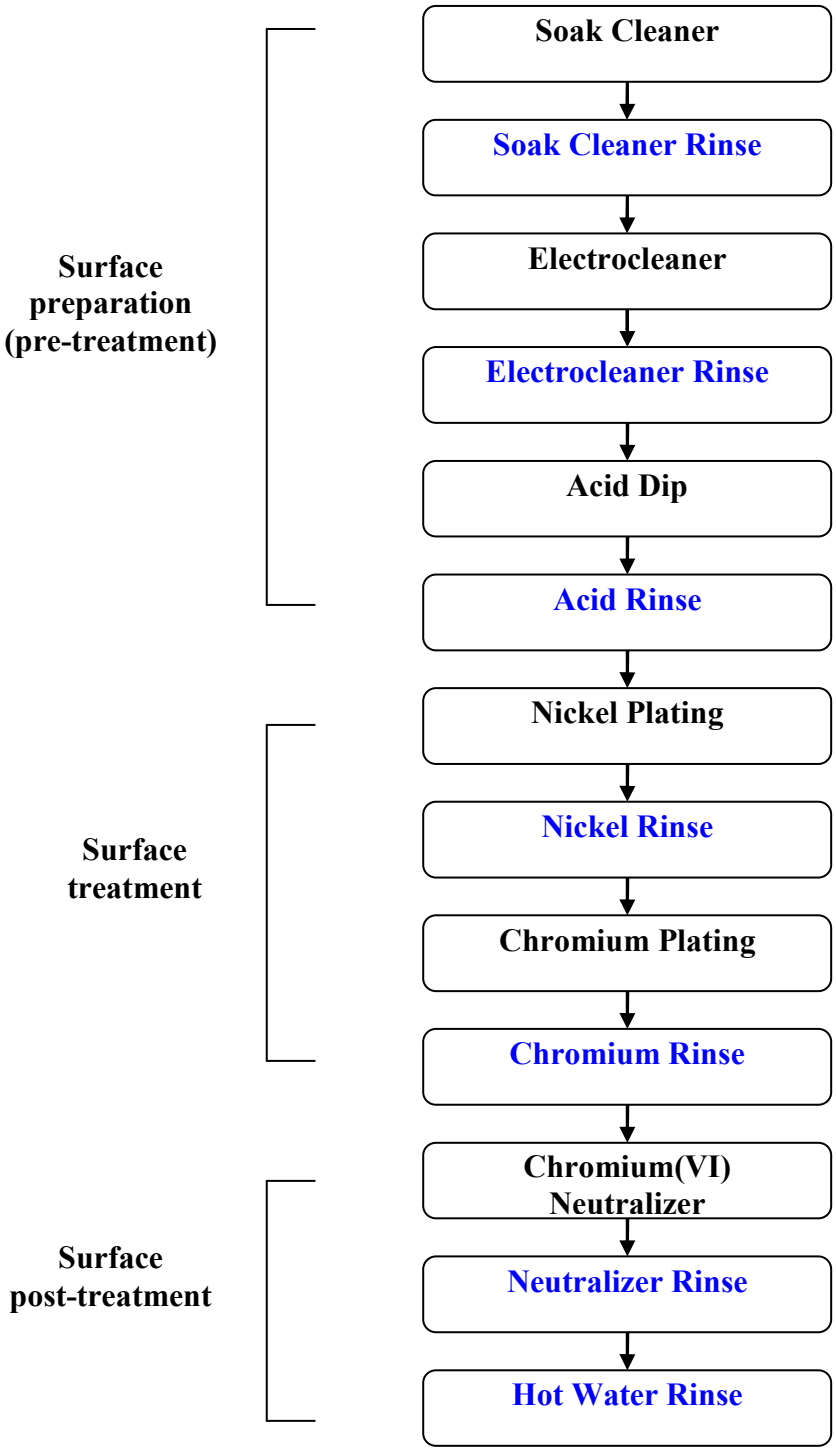


Figure 2.1 General electroplating lay out for chromium plating

Surface preparation involves cleaning the surface of the workpiece to remove greases, soils, oxides and other materials to prepare the surface for electroplating. The surface is first cleaned using alkaline detergents, solvents, caustics and other cleaners, this is followed by rinsing. The surface is then cleaned with an acid to remove oxides, and then rinsed.[6] Surface treatment involves the actual plating of the workpiece surface. This stage includes the plating solutions and rinses to achieve the desired finish.[6] The post-treatment stage includes any finishing operations on the workpiece surface after it has been plated. These processes can enhance the appearance or add to the properties of the workpiece.[6]

2.1.1 Rinsing in the Electroplating Process

Rinsing is an important process in the electroplating line and usually follows the process tanks.[7] Rinsing can be described as the substitution of the clinging film of process solution from the workpiece with an innocuous film of water.[8] It is essential to thoroughly rinse the workpieces between the various treatment stages for the removal of drag-out.[9] Drag-out is the term given to the process solution that remains on the workpiece and is transferred from the process tank into subsequent tanks.[10] Rinsing therefore prevents process solution accumulating on the workpiece and also prevents contamination of the subsequent process solutions. For example, if a workpiece contained an unrinsed film of alkaline cleaning solution, it would quickly contaminate the subsequent electrocleaner or acid pickle, which if left unrinsed would contaminate the plating bath. Proper rinsing is also required to prevent etching or precipitate reactions or any other reactions from occurring on the workpiece surface, which would be harmful to it and ultimately lead to an unattractive deposit.[8]

The rinse tanks that follow the process tanks can either be a static single rinse, flowing single rinse, flowing multiple rinse, static multiple rinse or counter-current rinse system.
Flowing rinse tanks have an inlet to allow fresh water to flow into the tank and an outlet for the water to exit the tank into the waste stream. The flow of water is continuous, to remove the contaminants in the rinse water. The water inlet is usually located on the bottom of the tank and the outlet is on the top of the opposite side of the tank. A single

stage rinse has one rinse tank, while a multiple stage rinse system has a series of rinse tanks one after the other.[7]

Countercurrent or cascading flow rinsing uses a series of connected rinsing tanks. The water inlet is through the rinse tank with the lowest concentration of chemicals (i.e. the one furthest downstream). The water overflow from this tank flows back into the previous rinse tank and then through the other rinse tanks in sequence. The water outlet is through the tank with the highest concentration (i.e. the first tank in the series). Since the same rinse water is re-used this method reduces the volume of water required.[7]

A static rinse tank has no water inlet or outlet, the rinse solution remains in the tank. This rinse needs to be dumped and refilled with fresh water to prevent the build up of contaminants and to prevent the rinse solution from becoming too concentrated.[7] A drag-out tank is a static tank that builds up a concentration of the process solution from the previous process tank. These tanks are usually positioned after the plating baths to collect the plating solution adhering to the workpieces (i.e. the drag-out).

2.2 Surface Preparation - The Pre-treatment Stage

In electroplating, the cleaning process within the pre-plating sequence is the most important consideration. This is because the appearance, adhesion and acceptance of the finished article depend primarily on a sound foundation for the final finish. This is achieved only with a clean and active substrate.[11] Plating onto a dirty or greasy surface leads to blistering or peeling of the deposit.[12,13]

Cleaning can be loosely defined as the removal of unwanted contaminants or dirt from a surface.[14] In the plating process the cleaning stage does not alter the surface physically or chemically.[11] A properly cleaned surface will remain the same as it was before cleaning, except for the missing dirt.[11,14] The cleaning process removes grease, oils and other soils left from the machining, stamping, spinning, pressing or polishing processing. Soil is matter out of place, and is anything that will interfere with the performance, long-term

reliability, final finishing or surface appearance if it remains on the product.[15,16] Soils can be classified as either organic or inorganic. Organic soils include oils, waxes and soaps. Inorganic soils may range from heat treat scale, weld scale, rust, smuts, oxide films, polishing compounds and shop dirt.[17,18,19] There are a variety of different approaches to cleaning, namely; alkaline soak cleaning, electrocleaning (electrolytic cleaning), solvent cleaning, ultrasonic cleaning and acid cleaning.

2.2.1 Alkaline Soak Cleaning

Alkaline soak cleaners remove the major portion of heavy oily soils quickly, effectively, safely and economically. The articles to be cleaned are submerged in the tanks containing the hot alkaline cleaning solution.[11,20] This step is followed by a water rinse. Alkaline cleaners are effective even on the most tenacious soils, the soils removed include oil, grease, waxy solids, metallic particles, carbon particles and silica.[21] The articles are cleaned by emulsification, dispersion, saponification or a combination of these mechanisms. These methods are explained below to better illustrate how the alkaline cleaners work.

2.2.1.1 Mechanisms of Cleaning

Cleaning is achieved using one or more of the six cleaning mechanisms namely, wetting, solubilization, complexing (sequestration), saponification, emulsification and dispersion (deflocculation).[14,22]

Wetting is vital to the removal of soluble and insoluble contaminants. In this mechanism, the cleaner with the aid of surfactants loosens the substrate-soil bond by the displacement of oil and the lowering of surface and interfacial tensions. Wetting agents reduce the surface tension of the cleaning liquid, allowing it to penetrate between the contaminant and the substrate (workpiece surface). Surfactants promote preferential wetting of the substrate thus allowing the cleaning agent to “wedge” its way between the contaminant and the substrate. The contaminant once separated from the substrate is then removed.[14]

Solubilization is the process whereby the solubility of a substance such as oil is increased in a certain medium e.g. water, by the proper selection of surfactants and/or co-solvents.[14]

In saponification a fatty compound reacts with alkaline salts in an alkaline cleaner to form a water soluble soap. Fatty soils are removed by dissolving them into the cleaning solution.[14,22]

Emulsification joins together two mutually insoluble liquids like oil and water; this is made possible by a surfactant. When the cleaner is dissolved in the water the water soluble end of the surfactant is solubilized in the water. Upon encountering the oil on the workpiece, the oil soluble end of the surfactant is immediately solubilized.[20]

In dispersion or deflocculation the surfactant acts to lower the surface tension of the cleaner at the surface of the workpiece. This allows the cleaner to cover the workpiece uniformly. The interfacial tension of the cleaner is lowered, allowing the cleaner to penetrate the oil film and break it into smaller units. As a result the oil is dispersed into smaller droplets that become suspended in the liquid cleaning solution.[20,22]

Complexing or sequestration is the mechanism where the undesirable ions, such as Ca^{2+} or Mg^{2+} or other heavy metals are complexed, preventing them from reacting with material that would form insoluble products on the surface of the workpiece . The ions form soluble complexes with the sequestering agents and are thereby removed from the workpiece.[14,22]

2.2.1.2 Alkaline Cleaner Composition

Alkaline cleaners are composed of three major types of components: [20,23]

- Builders
- Surfactants, and
- Organic or inorganic additives

Builders are the alkaline salts in the alkaline cleaner, and make up the largest portion of the cleaner. The salts are usually a blend selected from the following groups, alkali metal orthophosphates, alkali metal condensed phosphate, alkali metal hydroxides, alkali metal silicates, alkali metal carbonates, alkali metal bicarbonates and alkali metal borates. The alkali metal is usually sodium.[20]

The phosphates in the cleaners serve multiple functions. They provide a source of alkalinity and act as a buffer which prevents large changes in the level of alkalinity. In addition phosphates also have the ability to soften the water in the solution.[23,24] Ortho phosphates are used in heavy duty cleaners mainly to provide the required alkalinity. Tri sodium phosphate (TSP), Na_3PO_4, has a high alkalinity of pH 12.0 and is used in applications where a high degree of alkalinity and conductivity are required such as heavy-duty soak cleaners and electrocleaners. Condensed phosphates are used to a much greater extent. Sodium tripoly-phosphate (STPP), $Na_3P_3O_{10}$, is one of the most commonly used condensed phosphates, it provides a mild alkaline medium of pH 9.8, has good soil suspending properties and high sequestering abilities.[24]

Sodium hydroxide (caustic soda), NaOH, and potassium hydroxide (caustic potash), KOH, are the principle ingredients in most heavy duty soak cleaners and electrocleaners.[23,24] Their function is to saponify and emulsify heavy soils and to provide the appropriate alkalinity and a high conductivity, they also work with surfactants to disperse soils. Caustics have the highest degree of alkalinity to neutralize acidic soils present on workpieces.[24]

Silicates are used for their ability to saponify fatty acid esters that are common in greases and lubricants. They are usually used in conjunction with NaOH or orthophosphates. The silicates frequently used are hydrous or anhydrous metasilicates of sodium (SiO_2:Na_2O).[24]

Carbonates are used in milder alkaline cleaners. Carbonates possess good buffering qualities, which help stabilize the pH of the solution as it is cleaning.[23] The most popular

carbonate used is sodium carbonate (soda ash), Na_2CO_3. Bicarbonates are used when lower pH's are required for example aluminum cleaners.[24]

A surfactant can be defined as a linear molecule with a hydrophilic (polar) head and a hydrophobic (non-polar) tail[25] (see Figure 2.2). Surfactants are organic compounds which provide detergency, emulsification and wetting in an alkaline cleaner.[20] There are four major types of surfactants namely, anionic, cationic, non-ionic and amphoteric. Anionic surfactants carry a negative charge on the active portion of the molecule, and cationic surfactants have a positive charge on the active portion of the molecule. Nonionic surfactants have no electrical charge and amphoteric surfactants can be either anionic or cationic depending on the pH of the solution.[25] Examples of the different types of surfactants are given in Table 2.1.

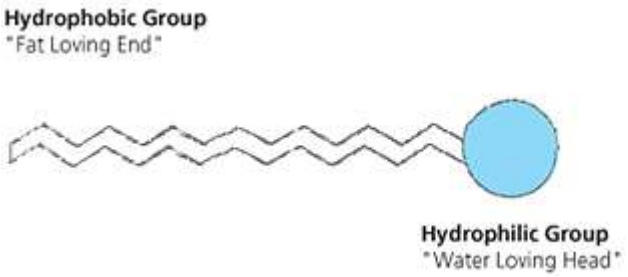


Figure 2.2 Structure of a surfactant molecule[26]

Table 2.1 Examples of anionic, cationic, nonionic and amphoteric surfactants [25]

Type of surfactant	Examples
anionic	sulfate esters, fatty alcohol sulfates, sulfated esters, sulfated fats and oils, sulfonic acid salts, aliphatic sulfonates, carboxylate soaps, lignosulfonates, phosphate esters, sulfated fatty acid condensation products, sulfocarboxylic acids/derivatives, alkyl glyceryl ether sulfonates, and miscellaneous sulfo esters and amides
cationic	imidazoline derivatives, betaines, pyridines, morpholines, and quaternary ammonium compounds
nonionic	polyoxyethylene-based materials, glycerides, block copolymers, alkanolamides, amine oxides, polyglycerides, polyglycerol and other polyol derivatives, glucosides, glycol esters, glycerol esters, polyglycosides, sorbitan esters (ethoxylates), alcohol ethoxylates, fatty amine ethoxylates, fatty acid ethoxylates, alkylphenol ethoxylates and sucrose esters
amphoteric	imidazoline derivatives, betaines, amine condensates, sulfobetains, quaternary ammonium compounds and phosphatides

The additives used in alkaline cleaners are either organic or inorganic compounds that provide additional cleaning or surface modification. Chemical compounds such as glycols, glycol ethers, chelating agents and polyvalent metal salts are examples of the additives used.[20]

The alkaline soak cleaners can be classified as light, medium and heavy duty. Light duty alkaline soak cleaners are composed of inorganic builders, wetting agents, buffering salts, sequestering agents, dispersants, inhibitors and occasionally solvents. They function by wetting, emulsifying, dispersing and solubilizing the soil. They are usually used for light soils. They differ from heavy-duty alkaline cleaners because they contain little or no caustic soda (NaOH) or caustic potash (KOH). The builders in light-duty alkaline cleaners are have a those yielding a pH range of 11.2 to 12.4.[11]

Heavy duty alkaline soak cleaners are composed of a balanced blend of highly alkaline builders, such as sodium or potassium hydroxide, along with carbonates and trisodium phosphate (TSP). They also usually contain silicates as dispersants and emulsifier's and sequestering agents such as sodium tripolyphosphate (STPP), tetrapotassium pyrophosphate (TKPP) and tetrasodium pyrophosphate (TSPP). Heavy duty cleaners have a high pH range of 12.4 to 13.8.[11]

Table 2.2 Typical operating constituents and chemical composition of light, medium and heavy duty alkaline cleaners [27]

Constituent	Light duty	Medium duty	Heavy duty
Caustic soda (NaOH) (g/L)	-	12.5	37.5
Soda ash (Na_2CO_3) (g/L)	-	25	25
Tribasic sodium phosphate ($Na_3PO_4.12H_2O$) (g/L)	25	12.5	6.2
Wetting agents* (g/L)	0.75	0.75	1.5
Sodium metasilicate ($Na_2SiO_3.5H_2O$) (g/L)	25	12.5	-
Temperature (ºC)	80-95	80-90	80-90

* the wetting agents also include surfactants

2.2.2 Electrocleaning

Electrocleaning also known as electrolytic cleaning is an integral part of the pretreatment process. Electrocleaners are basically heavy duty alkaline cleaners that are used with an electric current.[11,19] The different types of electrocleaning are anodic (reverse-current), cathodic (direct-current), periodic-reverse (PR) and interrupted-current (IR) cleaning.[28] These electrocleaning methods will be discussed in further detail below. Electrocleaners usually follow an alkaline soak cleaner and have two primary functions; they remove any residual soils that may have been left behind by the soak cleaner and they activate the metal surface. Activation is usually achieved by using anodic (reverse-current) electrocleaning.[11,17,19,28] The typical chemical composition and operating parameters for electrocleaners are given in Table 2.3

Table 2.3 Basic electrocleaning formulations and operating conditions[11]

Constituent	Metal substrate			
	Steel	**Copper**	**Brass**	**Zinc**
NaOH (%)	50	25	10	20
Na_2CO_3 (%)	4	23	38	28
Sodium tripolyphosphate (%)	5	10	10	10
Sodium metasilicate (%)	40	40	40	40
Wetting agent (%)	1	2	2	2
Temperature (°C)	80-95	70-80	60-70	70-80

In anodic electrocleaning the workpiece is actually made the anode, as a result gaseous oxygen (see Equation 2.1) is liberated at the metal surface. The oxygen bubbles liberated at the workpiece creates a scrubbing action which helps remove soils from the workpiece surface.[29] The oxygen gas bubbles rise to the top of the cleaner, increasing solution agitation and continually bringing fresh cleaning solution to the workpiece.[28]

In cathodic electrocleaning, the workpiece acquires a negative charge, and becomes the cathode. In direct current cleaning, hydrogen gas (see Equation 2.2) is evolved at the cathode (workpiece).[29] The workpiece is cleaned by the scrubbing action of the hydrogen gas bubbles.[29] The same equipment, voltage (3-12 V) and current densities (1-15 A/dm^2) are used for anodic and cathodic electrocleaning.[11,17,28]

$4\ OH^-\ (aq) + 4e \rightarrow 2H_2O\ (l) + O_2\ (g)$	*Equation 2.1*
$2H_2O\ (l) + 2e \rightarrow 2OH^-\ (aq) + H_2\ (g)$	*Equation 2.2*

Periodic-reverse electrocleaning, is a combination of anodic and cathodic electrocleaning. The workpiece is made alternately cathodic and anodic, using a voltage of 6-15 V.[28]

IR cleaning is based on the following theory, a reaction occurs at the interface between the soil on the workpiece and the cleaning solution. This reaction depletes the concentration of the cleaning chemicals at the interface. When the power is turned off momentarily, the reaction stops and the cleaner concentration is restored. When the current comes back on the solution concentration has returned to the optimum value at the interface. A typical cycle would be 8-9 seconds with current applied followed by 1-2 seconds with power off. [28]

2.2.3 Ultrasonic Cleaning

Ultrasonic cleaning is a method that uses high frequency sound waves to remove the contaminants on the workpieces.[30] The principle behind ultrasonic cleaning is cavitation.[31,32,33] The cavitation process occurs due to the constantly changing negative and positive pressures which cause the simultaneous formation and implosion of thousands of minute vapour bubbles (cavities).[30,32,33] The workpieces are cleaned by the formation and bursting of the vapour bubbles which have extreme pressures (approximately 10000 psi) and temperatures.[30,31] Ultrasonic cleaning offers many advantages such as, since it is based on sound it is inherently omnidirectional; ultrasonic cleaning solutions can be alkaline, solvent, acidic or neutral based; and effective cleaning can occur within cracks, pores and blind holes[31].

2.2.4 Solvent Cleaning

Solvent cleaning is the term given to using organic solvents for cleaning.[34] In solvent cleaning, the soil contaminants such as oil, grease, wax, asphaltic materials, resins and gums are easily solubilized by the solvent and removed from the workpiece.[34] The most widely used solvent cleaning processes are solvent vapour degreasing and cold cleaning.[12,19]

Cold cleaning is performed at, or slightly above room temperature. The workpieces are immersed and soaked in the solvent with or without agitation. The solvents commonly used are aliphatic petroleums, chlorinated hydrocarbons, chlorofluorocarbons or blends of these classes of solvents.[20]

In vapour degreasing the solvent is contained in a special unit which is provided with heating elements in the base and cooling coils round the top edge. The boiling solvent is condensed by the cooling coils and thus retained within the unit. When the component is placed in the vapour layer formed above the boiling liquid, the vapour condenses on the cold surface of the component and dissolves any soluble contaminants present. As the vapour condenses, the liquid drains back into the boiling liquid below, taking some of the soil with it. The cleaning process continues as more vapour condenses on the component. Once the temperature of the component reaches that of the vapour, condensation ceases and the cleaning process stops.[35] The most popular solvents for vapour degreasing are the chlorinated solvents; trichloroethylene, perchloroethylene and dichloromethane.[20,35,36] However, trichloroethylene is classified as a carcinogen and there are strict legislations governing its use.[35] Due to the health and safety issues and environmental aspects associated with the solvents used, there is an increased focus on the use of alternative solvents for solvent cleaning.[35] Some of the alternative non-chlorinated solvents are n-propyl bromide; hydrofluoroethers; alcohols; ethyl lactate, dibasic esters; glycol ethers; N-methylpyrrolidone; petroleum distillates, silicones and terpenes. [35]

2.2.5 Acid Cleaning

Acid cleaners are used for the removal of light grease, oxide films, scale and inorganic films. Acid cleaners, therefore differ from alkaline or solvent cleaners which are used for the removal of heavy grease and oil deposits. Acid cleaners are generally used in the final or near-final preparation of the metals prior to plating.[31] Acid cleaning has three main functions, firstly they remove any alkalinity left on the cleaned and rinsed metal surface, secondly acid cleaners remove oxide or tarnish films and lastly they provide an active and etched surface for good adhesion.[31] The presence of an oxide layer on the metal surface is particularly harmful as it negatively affects the adhesion of the electrodeposits to the metal surface and in an oxidised condition the metal surface is a poor conductor.[37]

There are two types of acid cleaning namely, acid dipping and acid pickling.[37] Acid pickling is most commonly used to clean steel and stainless steel metals. It is a more aggressive treatment than dipping.[20] A typical acid pickle bath contains inorganic acids such as hydrochloric, sulfuric, hydrofluoric and phosphoric; wetting agents and deflocculents. Acid dipping baths usually contain an inorganic acid and wetting agents.[37]

Table 2.4 Typical composition of acid cleaners for dipping[37]

Metal substrate	Concentration			
	Sulfuric acid (%v/v)	Fluoride (g/L)	Persulfate (g/L)	Wetters (g/L)
Brass	3-5	1.5-3	-	0.075-0.225
Copper and Alloys	2-4	-	7.5-22.5	0.075-0.225
Zinc Alloys and Castings	1-2	0.75-2.25	-	0.075-0.225

2.3 The Electroplating Stage

Electroplating is performed in a liquid solution containing dissolved salts of the metal to be deposited. This solution is called an electrolyte. The workpiece to be plated is immersed into the electrolyte solution and is made the cathode by connecting it to the negative lead of a rectifier. A rectifier provides the current for the system and converts alternating current (ac) to regulated low voltage direct current (dc).[39] To complete the electrical circuit anodes are immersed in the solution and these are connected to the positive lead of the rectifier. The anode is usually made of the plating metal and when current passes the metal is dissolved from the anode into solution (oxidation of the solid anode). In some cases for example chromium plating an inert anode is used to complete the circuit and allow current to flow. When current flows the plating metal ions migrate to the cathode where the positive charge on the ions is neutralized by the excess electrons present and the metal atoms are removed from the solution and are deposited on the surface of the cathode (workpiece) as a thin layer (reduction of the ions).[40]

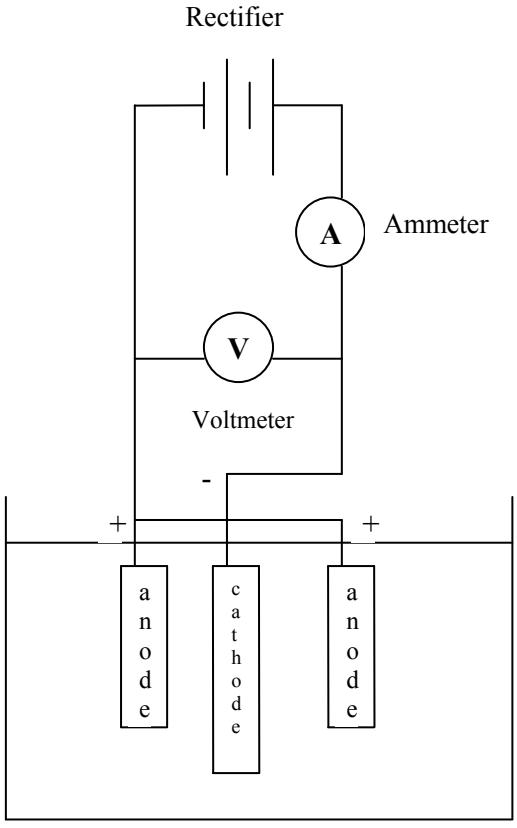


Figure 2.3 A simplified electroplating set up

2.3.1 Equipment used for the Electroplating Process

The plating line can either be automatic or manual. A manual plating line is usually employed when the output is fairly small or a wide variety of different finishes are required on a range of articles. For a large output of articles, especially articles that are required to be processed to a uniform finish, an automatic plating line may be employed.[12]

The articles to be treated are moved along the plating line either in barrels or are held on frames called jigs or racks.[27] When a number of similar articles are to be plated, a plating jig or rack is usually used. A plating jig holds the workpieces in position while being treated on the plating line and is able to conduct current from to the workpieces.[41] A number of wire springs contacts are arranged on the jigs to mount the workpieces. Once the workpieces are then hung on the jigs the whole jig is immersed in the appropriate solution. The jigs are designed to hold the workpieces in the most advantageous position for plating significant surfaces, and are made a convenient size so that they can be easily handled by the plating operator.[27,41,42] The jig is generally constructed of brass or copper and is covered with a suitable insulating material such as the commonly used polyvinyl chloride (PVC). Copper is the most widely used material to construct the jigs as it offers a number of advantages. The advantages of using copper are its high electrical conductivity, strength, absence of hot shortness, ease of bending, and its ease of low temperature soldering.[41,42]

Barrel plating is usually used in bulk finishing for small uniform workpieces. Articles such as screws, nuts, washers etc. are usually plated in barrels. There are two main types of barrels, the horizontal immersed barrel and the oblique tilting barrel.[43] Barrels are usually constructed of polypropylene and PVC.[4] Barrel plating typically involves a rotating perforated vessel that tumbles the contained workpieces. The barrel is immersed in the solutions of the plating line, while tumbling the workpieces.[43] The process and rinse solutions enter and exit the barrel through holes drilled along each side of the barrel. The exterior of the barrel is shaped like a hexagon to provide a pumping action so solution can be replenished as the barrel rotates. The anode is located outside the barrel,

while the cathode is inside. The most common method to supply current to the workpieces inside the barrel is by using a dangler.[1,39,44] This is usually a coated cable with a large metal ball crimped onto the end which terminates inside in the barrel. The metal ball makes contact with the top of the workpieces as they tumble. As the parts move they make or break electrical contacts creating a bi-polar effect. The bi-polar effect means that the entire surface of the workload which is in the current path at any time is in cathode contact. The cable enters through a hole at each end of the barrel and is connected to the rectifier.[44]

The process solutions and rinse solutions used on the electroplating line are contained in vats or tanks. These tanks should hold the solutions without suffering attack which will cause contamination and leakage, and must be able to withstand the operating temperatures.[4] The materials which meet these requirements and are used to construct the tanks include polypropylene, steel, stainless steel and PVC.[4,12,45] The tanks can also be lined, the inside liner protects the chemical solution while the outside tank provides the mechanical support.[4] The most widely used lining materials are rubber and plastics (PVC, polypropylene and polyethylene).[4,12,45]

The electroplating bath or tank (see Figure 2.4) consists of the following components:[2,46]

- The rectifier, which supplies the direct current (dc) to the plating tank.
- The negative electrodes or cathodes, this is the workpiece to be plated.
- The plating solution or electrolyte solution, containing the metal to be plated in a soluble form.
- The positive electrodes or anodes, there are usually made from the metal being plated, or sometimes inert or insoluble anodes.

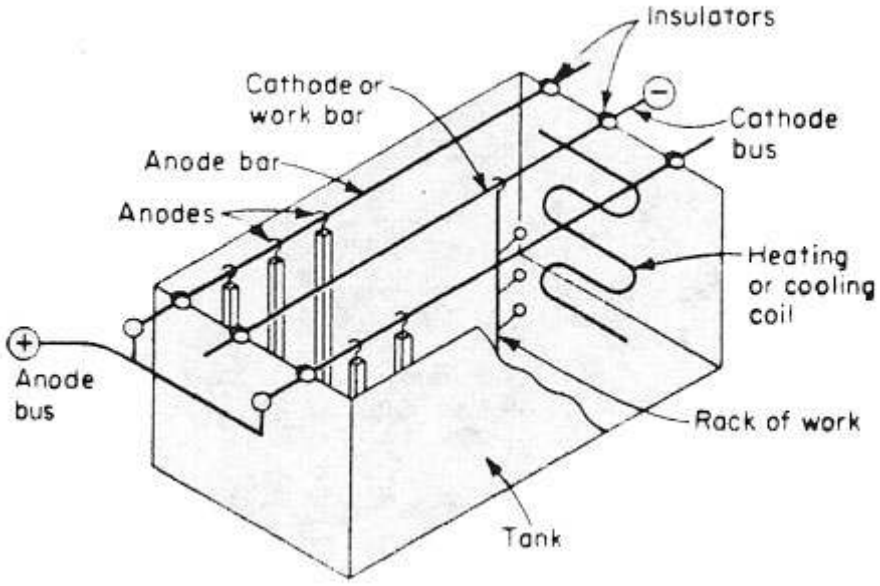


Figure 2.4 A typical electroplating tank [46]

The plating tank has conductors running along its length; these are referred to as bus bars. The outside bars are the anode bus bars and they are connected to the positive side of the rectifier. The anodes are hung on these bars. The central bus bar is the cathode bar and is connected to the negative side of the rectifier, this bar holds the workpieces.[46]

The anodes serve two purposes, firstly they are used to complete the electric circuit and secondly when a soluble anode is used it replenishes the metal content removed during the plating process.[4] There are two types of anodes used in electroplating, soluble and insoluble anodes. Soluble anodes are made of the metal to be deposited, while insoluble anodes are made of inert material.[1,4,12] The anode material must be free from any impurities which may result in contamination of the electroplating solution, be co-deposited on the cathode, react with constituents in the plating solution or form an insoluble sludge upon the anode surface. The anodes should be in a suitable metallurgical condition to ensure that it dissolves uniformly. Anodes are usually in the form of flat or oval strips which are suspended from hooks, or small pieces of the metal are contained in baskets.[12]

2.4 The Electrochemistry in the Electroplating Process

2.4.1 Faraday's Laws of Electrolysis

When electrolysis is carried out in the plating solution, the metal is being deposited on the cathode. The extent of the metal deposited on the cathode is determined by the quantity of electricity passed. This relationship is given by Faraday's laws of electrolysis shown below.[4,5]

1) The weight of metal deposited at the cathode is proportional to the quantity of electricity transferred at that electrode.
2) When the same quantity of electricity is passed through several solutions in series the amounts of the metals deposited are proportional to the chemical equivalents weights of the respective metals.

The mass (w in g) of the metal deposited is given by:[4]

$$w = \frac{It}{96500} \times \frac{A}{z} \qquad \textit{Equation 2.3}$$

Where I : is the current passed (A)
t: is the time of deposition (s)
A: is the atomic weight of the metal (g mol^{-1})
z: is the charge of the ion

These laws are fundamental to electroplating, however apparent deviations from Faradays laws are noticed in practice. The causes for these deviations include unproductive simultaneous reactions e.g. hydrogen gas formation or deposition of impurities.[4]

2.4.2 Current Efficiency

In plating operations the entire current is not always utilized for the electroplating process. Some of the current is wasted on side reactions also taking place. For example in nickel and to a much greater extent chromium plating the current is used for hydrogen gas evolution. Current efficiency or cathode efficiency is the percentage of the total current usefully employed for the cathodic deposition of the metal.[4] Typical values for the cathode efficiency in nickel and chromium plating solutions are given in Table 2.5.

Table 2.5 Cathode efficiencies of nickel and chromium plating baths[4]

Metal	Type of bath	Cathode Efficiency (%)
Cr	Chromic acid	12-16
Ni	Sulfate-chloride	94-98

2.4.3 Polarization

When an electrode (either anode or cathode) is immersed in an electrolyte with no current flowing, a potential difference exists between the electrode and the electrolyte. This potential difference is called the static or steady state electrode potential [Es]. When a particular metal is immersed in an aqueous solution of its ions of unit molar activity at 25º C, this potential is called the standard reduction potential [E°] for that metal.[12]

The equilibrium potential or voltage for the reduction reaction of a metal (see Equation 2.3) at the electrode is given by the Nernst Equation[5] (see Equation 2.4).

$$M^{n+} + ne^- \rightarrow M \qquad \textit{Equation 2.3}$$

$$E = E^o + \frac{RT}{nF} \ln[M^{n+}] \qquad \textit{Equation 2.4}$$

E = Electrode potential, V

E^o = Standard reduction potential, V

R = gas constant, 8.314 J/Kmol

T = Temperature, K

n = number of electrons per mole of oxidized form

$[M^{n+}]$ = concentration of the oxidized metal, mol/L

In practice however the operating voltage of the plating bath required to deposit a metal plate onto the workpiece is greater than the potential calculated using Equation 2.4. When two electrodes are connected (in series) with an external electromotive force, the potentials are displaced from their steady state value. The potential of the cathode becomes more negative and the anode becomes more positive, the decomposition potential is reached, current begins to flow and irreversible electrode reactions occur at a finite rate. The metal is deposited, or hydrogen gas released at the cathode and at the anode dissolution occurs or oxygen gas is released. When these processes take place at an electrode and its potential [Ep] departs from the static value, that electrode is said to be polarized.[4,12] The factors that cause an electrode to depart from [Es], its unpolarized value, to [Ep] its polarized value are:[4,12]

n_{conc} - concentration overpotential

n_{act} - activation overpotential

n_{ohmic} - ohmic overpotential

Then:

$$Ep = Es + n_{conc} + n_{act} + n_{ohmic} \qquad \textit{Equation 2.6}$$

$n_{Total} = Ep - Es$, which is negative for cathodic processes and positive for anodic processes.

Polarization is therefore the phenomenon whereby an extra potential has to be applied to carry out the plating process. The three factors (see Equation 2.6) that contribute to the overpotential are ohmic, activation and concentration overpotential.

2.4.4 Cell Voltage

The voltage that must be applied between the anode and cathode of the electroplating tank (vat) to produce a finite current is called the cell voltage. The cell voltage is dependent on a number of factors shown in Equation 2.7 below:[12]

$$V = E_{cell} + \text{total cathodic polarization} + \text{total anodic polarization} + IR$$

Equation 2.7

Ecell is the minimum voltage needed to cause the electrode reactions to take place and plating to commence. This potential is equivalent to the decomposition potential. The anode and cathode polarization oppose the applied voltage therefore they are both added to the Ecell. The IR drop, or resistive overpotential is the basic Ohm's law voltage drop across the cell derived from the current I and the resistance, R, of the electrolyte.[12]

2.5 Nickel Plating

Nickel plating is primarily used as an undercoat for decorative chromium plating.[9,12,47,48] The nickel deposit protects the base metal and the chromium deposit provides a non-tarnishing, wear-resistant surface.[12] The nickel and chromium plating system provides a highly lustrous and corrosion protective finish for articles of steel, brass, zinc die castings and aluminium and magnesium alloys.[4,5,49,50]

In 1916, Professor O.P. Watts formulated and published the formula for a nickel bath, which has stood the test of time, and is till today used with little modification in most commercial electroplating operations.[3] The basic composition of the Watts nickel bath is nickel sulfate, $NiSO_4.7H_2O$ (240 g/L), nickel chloride, $NiCl_2.6H_2O$ (20 g/L) and boric acid, H_3BO_3 (20 g/L).[3,48] In the Watts nickel bath, nickel sulfate is the main ingredient in the solution, it is used as the principal source of nickel ions. This is because it is readily soluble, relatively cheap, commercially available and is a source of uncomplexed nickel ions.[3,48,51] The chloride ions serve two main functions, they assist in anode corrosion and increases the cathode efficiency.[3,5,48,51] Boric acid functions as a buffering agent, in order

to maintain the pH of the solution. Most nickel solutions operate over a range of pH 1.5 to 5.[48] The anodes used are soluble nickel anodes, in the plating baths the anodes are usually enclosed in cotton or polypropylene bags. This prevents fine particles from entering the solution and contaminating the plating solution and cathodes surface.[3,5,12,50] The chemical composition and operating conditions of the different nickel plating solutions are shown in Table 2.6.

Table 2.6 Typical composition and operating conditions of nickel plating baths[20,50]

Parameter	Watts bath	Sulfamate bath	Fluoborate bath	All Chloride bath
Nickel sulfate, $NiSO_4.6H_2O$ (g/L)	225-410	-	-	-
Nickel chloride, $NiCl_2.6H_2O$ (g/L)	30-60	0-30	0-15	300
Nickel sulfamate, $Ni(SO_3NH_2)_2$ (g/L)	-	263-450	-	-
Nickel fluoborate, $Ni(BF_4)_2$ (g/L)	-	-	225-300	-
Boric acid, H_3BO_3 (g/L)	30-45	30-45	15-30	37.5
pH	1.5-5.2	3-5	2.5-4	4.0
Temperature (°C)	46-71	38-60	38-71	60
Current density (A/dm^2)	1-10	2.5-30	2.5-30	4.3

The different types of nickel deposits include bright nickel, semi-bright nickel and satin nickel. Bright nickel deposits produce a highly lustrous, reflective finish to the article, a semi-bright nickel deposit produces a partially bright finish and a satin nickel deposit is used when a matt, dull finish is required.[50,51]

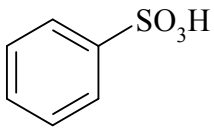
2.5.1 Organic compounds used in Nickel Plating

Bright nickel plating produces workpieces that have a high degree of brightness, reflectivity and levelling. Levelling agents known as levellers, modify the nickel deposit such that any minor surface defects such as scratches and polishing marks are filled.[3] If a final bright appearance of the workpiece is required, the nickel plating solution contains organic as well as inorganic constituents.[48]

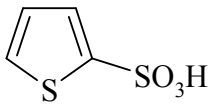
The organic compounds used include brighteners, levellers and stress relievers. The organic chemicals available usually serve a dual purpose, for example a brightener can

also have levelling properties, or a stress reliever may also assist in the brightening action.[3]

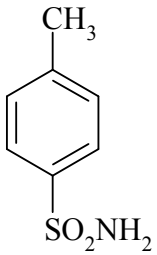
There are two classes of brighteners namely brighteners of the first class and brighteners of the second class. Brighteners of the first class do not produce a fully bright finish when used alone. They are usually used together with second class brighteners, which produce a synergistic effect.[3] Brighteners of the second class have the ability to obtain a fully bright deposit. However they cannot be used on their own, as they have a harmful effect on the physical properties (cause brittleness and induce tensile stress in the deposits) at high concentrations.[3] First class brighteners can be used at high concentrations and do not have a marked effect on the physical properties of the deposit. Therefore, when these two classes of brighteners are used together, a lower concentration of second class brighteners is required thereby reducing their harmful effect.[3] Compounds of the first class have the following characteristic group, $=C\text{-}SO_2$ in the molecule.[1,3,47,52] Examples of these brighteners are given in Figure 2.5.[3]



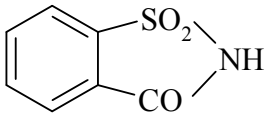
A) Benzene sulfonic acid



B) Thiophen-2-sulfonic acid



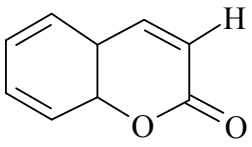
C) p-toluene sulfonamide



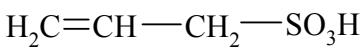
D) *o*-benzoic sulfonimide (saccharin)

Figure 2.5 Examples of first class brighteners

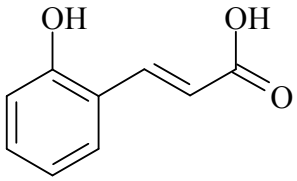
Brighteners of the second class have an unsaturated group present in the molecule. They are characterized by unsaturated groups such as: C=O, C=C, C≡C, C=C-C-O, C≡N, N=N and N-C=S.[1,3,52] Figure 2.6 shows examples of these brighteners.[3]



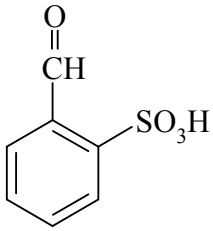
E) Coumarin



F) Allyl sulfonic acid



G) *o*-hydroxy cinnamic acid



H) *o*-sulfo benzaldehyde

Figure 2.6 Examples of second class brighteners

The concentrations of brighteners in the nickel baths range from approximately 1 to 25 g/L for either first class brighteners or a combination of first and second class brighteners. Brighteners of the second class are generally used in concentrations of 0.005 to 0.2 g/L.[20] For example naphthalene polysulfonic acid a first class type brightener is used in concentrations of about 15 g/L and aromatic sulfonamides or sulfonimides are usually present at around 2g/L. Acetylenic compounds, a type of second class brighteners, are only present at concentrations of about 0.01 g/L.[3]

A popular levelling agent is coumarin, which is also a second class brightener. Other good levelling agents are sulfobetaines, an example is pyridinyl sulfonic acid.[3] Stress relievers are added to nickel baths to counteract the deleterious effect of second class brighteners.[3] A commonly used stress reliever is saccharin which also serves as a brightener of the first class.[3,47]

2.6 Chromium Plating

Electroplated chromium deposits rank among the most important plated metals.[53] There are two types of chromium plating namely decorative and hard chromium plating.[54,55] The difference between hard and decorative plating is the thickness of the deposit.[20] In decorative plating the deposit thickness is usually between 0.2 and 0.5 μm.[9,12,56] Hard chromium plating has a thicker deposit usually ranging between 2.5 and 500 μm.[9,20,54,56] The chromium plating system used for the electroplating line studied in this dissertation is decorative plating. Decorative chromium plating is used for their protective and decorative characteristics. The deposits offer a pleasing, reflective appearance while also providing a durable and corrosion resistant metal surface.[49,53,54]

Chromium is usually deposited from an aqueous solution of chromium trioxide (chromium anhydride) CrO_3, most plating literature refers to solid chromic trioxide as its hydrated form, chromic acid.[3,53,55] In this dissertation CrO_3 will also be referred to as chromic acid. Chromium cannot be deposited from a bath containing only chromic acid, an acid catalyst must also be present to aid in the cathodic deposition of chromium.[3,5,49,53] The commonly used catalyst is sulfate (SO_4^{2-}), the source of sulfate ions is sulfuric acid.[20,49,53]. In the absence of the sulfate catalyst the deposit contains oxides of chromium and is multicoloured resembling a rainbow.[52,57,58] The ratio of chromic acid to sulfuric acid is very important in the chromium plating baths. The ratio usually falls within the range of 80:1 to 120:1, with 100:1 being the preferred ratio.[1,3,9,20,49,53] Too low amounts of catalyst (i.e. high ratios) can result in either no current flow, no plating or brown oxide stains and too high catalyst concentrations (i.e. low ratios) can cause partial plating with poor throwing power or no plating at all.[5,53,57] Throwing power is the ability of a bath to uniformly deposit metal on the cathode surface.[53,57] A second catalyst usually the fluosilicate ion (SiF_6^{2-}) is sometimes used in chromium plating baths in order to improve the current efficiencies, throwing power, and current densities.[1,20,53,49] The typical chemical composition and operating conditions for decorative and hard chromium plating baths are given in Table 2.7.

Chromium plating uses insoluble anodes.[2,5,12] The main reason for using insoluble anodes is that chromium metal dissolves with a much higher anodic efficiency (85-100%) than cathode efficiency (12-24 %).[1] This results in the chromium concentration of the bath rapidly increasing. The most commonly used insoluble anodes are usually lead-tin, lead-antimony or lead alloys.[2,3,5,55] Lead anodes are advantageous as they reoxidise Cr(III) to Cr(VI) at the anode surface and provide effective current distribution.[1,20,53]

Table 2.7 Typical bath conditions for decorative and hard chromium plating[20,54,59]

Condition	Decorative	Hard
Chromic acid (g/L)	200-400	250-400
Chromic/sulfate ratio *	80 to125:1	75 to 100:1
Current density (A /dm^2)	7.5 - 17.5	22-100
Temperature (°C)	32 - 50	43-63

* chromic acid to sulfuric acid weight ratio

2.6.1 Deposition of Chromium

The chromium plating baths are simple, however the mechanism of chromium deposition from chromic acid is more complicated and not fully understood.[52,53] This is due to the chromium being present in the form of complex anions ($Cr_2O_7^{2-}$) and being able to exist in several oxidation states (e.g. +6, +3 and 0) being the most common.[3,53]

The theory involved in the electrodeposition of hexavalent Cr(VI) is very complex and a number of theories have been proposed to try to explain the mechanism of Cr(VI) electroplating. Most theories follow the various reaction sequences presented below:[49,52,60]

$$CrO_3 + H_2O \rightarrow H_2CrO_4 \rightarrow CrO_4^{2-} + 2H^+ \qquad \textit{Equation 2.8}$$

$$2H_2CrO_4 \rightarrow H_2Cr_2O_7 + H_2O \rightarrow Cr_2O_7^{2-} + 2H^+ + H_2O \qquad \textit{Equation 2.9}$$

The deposition reaction is:

$$Cr_2O_7^{2-} + 14H^+ + 12e \rightarrow 2Cr + 7H_2O \qquad \textit{Equation 2.10}$$

This reaction occurs in the presence of the catalyst. The standard redox potential for the above deposition reaction (Equation 2.10) is +0.4 V (vs SHE).[5] However a higher voltage usually between 4-10 V [3,5,53] is used in the actual electroplating processes as chromium plating has a low cathode efficiency.

In addition to the desired reactions, two side reactions also take place. The side reactions that occur are shown below:[49,60]

$2H^+ + 2e \rightarrow H_2\,(g)$	*Equation 2.11*
$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$	*Equation 2.12*

The hydrogen ions react to form hydrogen gas. In chromium plating 80-90 % of the power is used by this reaction. This results in a high quantity of hydrogen gas at the electrode surface.[49,60] The second reaction leads to the formation of Cr(III) ions.

The concentration of the Cr(III) ions is controlled by the reactions occurring at the lead anode. The reactions taking place at the anode are shown below:[49,60]

$4OH^- + 4e \rightarrow 2H_2O + O_2(g)$	*Equation 2.13*
$Pb + 4OH^- + 4e \rightarrow PbO_2 + 2H_2O$	*Equation 2.14*
$2Cr^{3+} + 3O_2(g) + 6e \rightarrow 2CrO_3$	*Equation 2.15*

O_2 gas is evolved from the anode surface as shown in the above equation (Equation 2.13). This reaction consumes most of the electric current.[49,60] The second reaction (see Equation 2.14) shows the formation of a lead peroxide coating on the anode surface. This coating is very important as it is essential for the last reaction (the oxidation of Cr(III) to Cr(VI)) to occur.[52] High Cr(III) concentrations can be harmful to the plating process, usually a maximum concentration of 7.5 g/L of Cr(III) can be tolerated in the plating bath.[61] Higher concentrations may inhibit the deposition process.[61]

2.6.2 Monitoring the Chromium Plating Baths

The chromic aid concentrations in the plating baths can be monitored and maintained by making frequent density measurements.[49] Density tests are used as a rough field measurement of the chromic acid concentration of the plating bath since the density is related to the concentration of the solute. The density of the bath is measured in either degrees Baumé or specific gravity with a hydrometer. This gives an approximate concentration of the chromic acid level in the bath.[46]

CHAPTER 3

INTRODUCTION TO WASTE MINIMISATION IN THE ELECTROPLATING INDUSTRY

3.1 Waste and Waste Minimisation

Waste can be defined as an undesirable or superfluous by-product, emission, or residue of any process or activity which has been discarded, accumulated or stored for the purpose of discarding.[62]

Liquid, solid and gaseous waste materials can be generated during the manufacture of any product. The wastes produced not only create potential environmental problems but also represent losses from the production process of valuable raw materials and energy.[63]

An industrial process is an activity which converts the inputs into outputs. The inputs of a process include raw materials, resources (energy and water), consumables and packaging. The outputs of the process are the desired final product and waste.[64] Waste can be classified as anything that does not end up in the final product.[65]

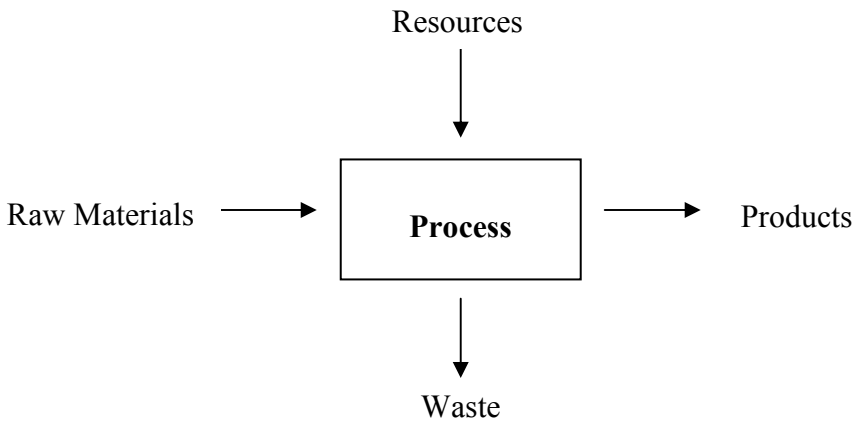


Figure 3.1 A general model of a process flow diagram[64,66]

The wastes produced can take many forms including:[63,64,65,67]

- liquid and solid residue from a process
- raw materials not included in the final product
- water (rinse water)
- effluent
- waste oils and solvents
- gaseous discharges
- heat/energy losses
- rejects and rework
- by-products of a process
- wasted effort

The wastes generated from the electroplating industry include volatile organics, acid/alkali fumes, hexavalent chromium, nickel, waste water containing metals, oils/greases, and sludge and process solutions with high metal contents.[68,69]

Waste minimisation is defined as reducing or preventing the generation waste at its source.[63,67,70,71,72] Waste minimisation is achieved through efficient use of raw materials, energy and water, and by understanding and changing processes to reduce and prevent waste.[64,70] Synonymous terms for waste minimisation include waste reduction, clean or cleaner technologies, pollution prevention, environmental technologies and low and non-waste technologies.[63,73] Waste minimisation options cover:[66]

- raw material and ingredient use
- product loss
- water consumption and effluent generation
- paper and packaging
- factory and office consumables
- energy consumption
- all other solid, liquid and gas wastes
- wasted effort

Waste minimisation is beneficial to a company as it helps improve the company's production efficiency, profits, product quality and environmental performance. The implementation of waste minimisation has helped many organizations reduce:[64,65,66,74,75,76,77]

- the quantity and toxicity of hazardous and solid waste generation
- raw material and product losses
- raw material purchase costs
- compliance violations
- environmental liability
- waste management costs
- workplace accidents and exposure

Therefore implementing waste minimisation options in an organization, results in increased output, reduced processing time and less waste. All these ultimately lead to financial savings for the company.

The waste management hierarchy (see Figure 3.2) identifies waste disposal options and ranks them in order of increasing environmental impact. The hierarchy shows that waste disposal has the greatest impact on the environment and is typically the least cost-effective waste management solution for a company. By moving up the hierarchy a company could save money, raw materials, water, energy, reduce its impact on the environment and improve its image.[78] The waste management hierarchy shows the order of preference of reducing waste and emphasizes that prevention or elimination of waste is better than trying to find a cure.[67]

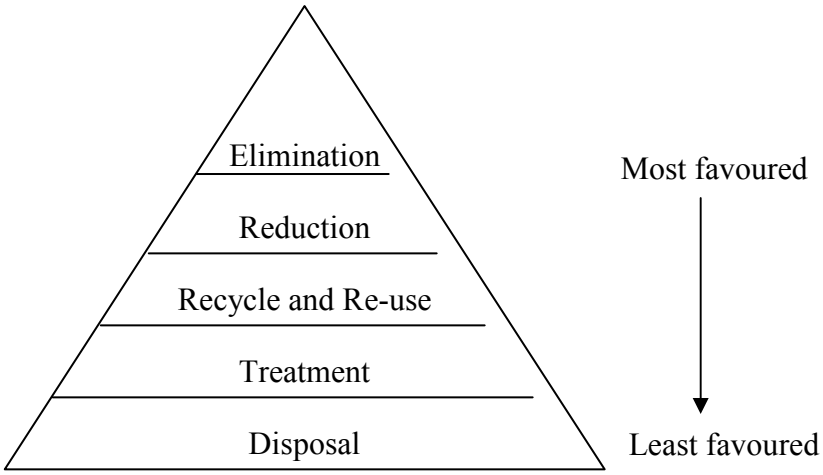


Figure 3.2 The waste management hierarchy[63,64,67,72,73,78]

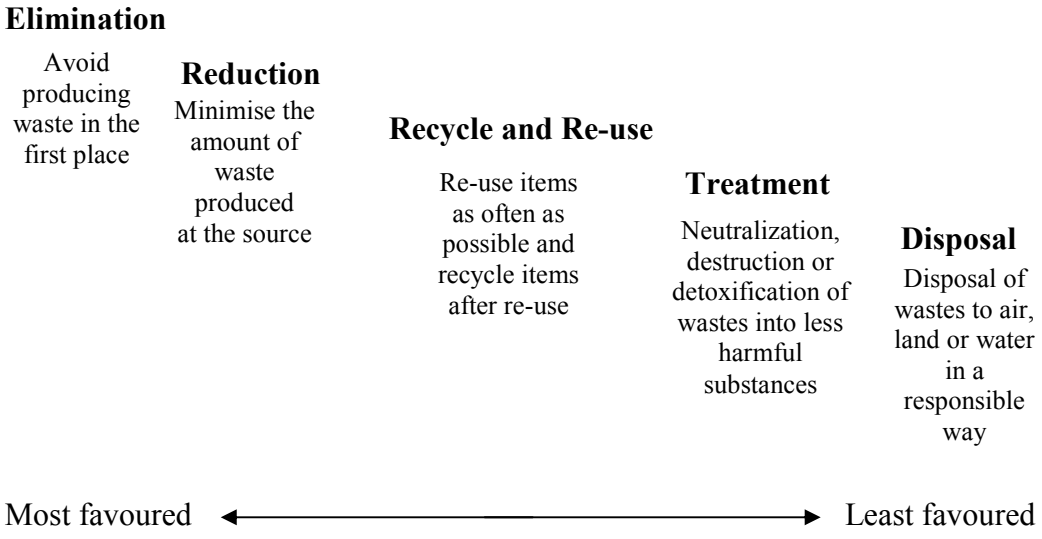


Figure 3.3 An explanation of the different steps in the waste management hierarchy[63,67,78]

The principles fundamental to good waste minimisation practices are illustrated in the waste management hierarchy. Waste minimisation is primarily concerned with the elimination, reduction and recycle-reuse steps of the hierarchy.[63,70,79] The elimination step involves the complete prevention of waste. The reduction step reduces the generation of waste at the source, and also refers to any practice that reduces the use of hazardous materials in the production process.[63,69] Recycling and re-use involves the reuse or recovery of raw materials or materials generated as by-products that can be processed further on-site or sent off-site to reclaim its value.[80] The treatment of wastes should be

considered once elimination, reduction and recycle-reuse steps have been investigated. The disposal of wastes should be the last option, and should be disposed of in a responsible manner.[67]

3.2 The Waste Minimisation Programme

Waste minimisation can be implemented through the use of a waste minimisation programme, which is a systematic planned procedure to help identify ways to reduce or eliminate waste.[79] A step-by step action plan for implementing an effective waste minimisation programme is outlined in Figure 3.4.

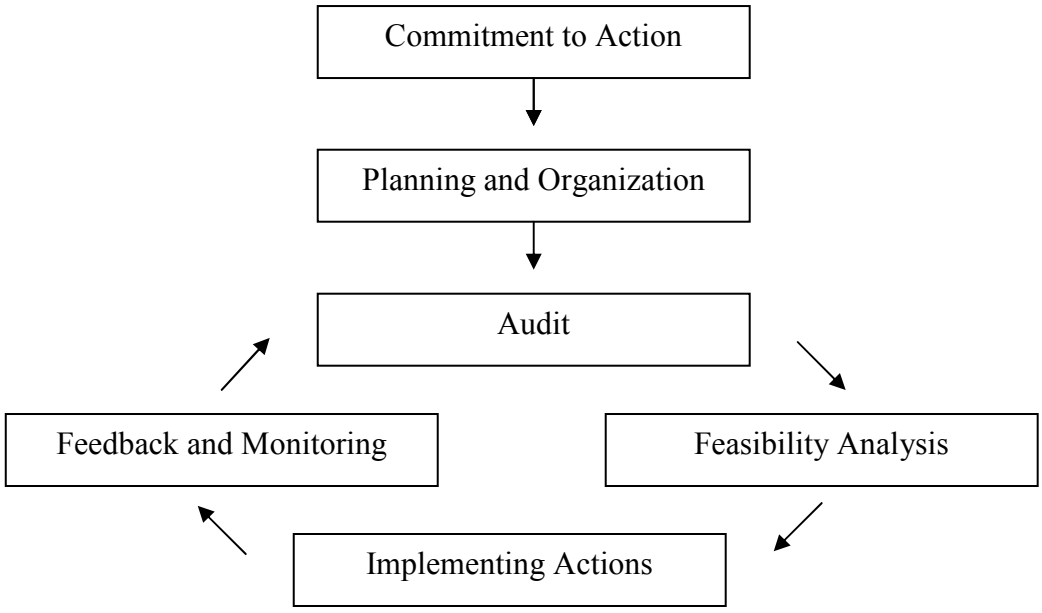


Figure 3.4 The steps involved in implementing a waste minimisation programme[63,79,81,82,83,84]

The first step in a waste minimisation programme is to obtain commitment from management. It is essential for the success of the waste minimisation programme that the most senior management within a company take a leading role. The next step in the programme is planning and organization. The essential elements of planning and

organizing are setting waste minimisation goals, and organizing an assessment programme task force.[63,79,83]

The third step is the audit step also referred to as the assessment phase. The audit step is a systematic procedure for identifying waste minimisation options to reduce or eliminate waste. This step involves a number of process stages. The stages include the collection of process data and facility data, prioritization and selection of assessment targets, data review and site inspection, selection of an assessment team, identification of significant waste generation practices, and the screening and selection of waste minimisation options for the feasibility study.[63,79,83] The waste minimisation audit step will be discussed in detail in the next section.

The feasibility analysis step involves an economic and technical evaluation. In order to implement a waste minimisation option it must be shown to be economically and technically feasible. A technical evaluation determines whether a proposed option will work in a specific application.[63] The process and equipment changes both need to be assessed for their overall effects on waste quantity and product quality. An economic evaluation is carried out using standard measures of profitability such as payback period, return on investment and net present value.[63,83] The next step is implementation. A waste minimisation option that will prove to be both economically and technically feasible should be implemented.[83]

In order to determine whether the anticipated waste reductions were achieved it is essential to measure and evaluate the results of the implemented changes. The feedback process is therefore necessary for the maintenance of a waste minimisation programme. This process involves the collection of information and data at frequent intervals, to identify the accomplishments and status of the waste minimisation options.[63]

3.3 Waste Minimisation Audit Stage

The waste minimisation study reported in this dissertation involves an audit of an electroplating plant in terms of material wastage and indentifies some potential waste minimisation options. In studies of this type, the data on the composition and flow rates and cost of the process streams must be collected. The relevant information acquired can be put together into a process description; which can be represented in a process flow diagram (see Company and Process Profile in Chapter 5). This data can then be analysed using established waste minimisation audit techniques, to determine the composition, quantity and cost of the waste streams and to identify potential waste minimisation opportunities for the company. The waste minimisation techniques include a Scoping Audit, Mass Balance Analysis, True Cost of Waste Analysis and Monitoring and Targeting. These assessment techniques are discussed in detail in this section.

The audit step includes the collection of data required for the waste minimisation programme. This involves a site inspection, which helps to understand the process plant thereby identifying and characterizing all waste streams. The required data can be collected by performing a "historical" audit and a "live" audit.[64] A historical audit involves the collection and analysis of existing data. The data for a historical audit can be gathered from invoices, production logs, process specifications and bills.[63,64,66] This provides an understanding of how resources are consumed and gives the opportunity to carry out a simple understanding of material use, which will help identify any inefficiencies.[64] For this project, the historic or existing data was collected from product information, discussion with the plant owners and employees, analysis reports of the plating and cleaning tanks from the chemical supplier, Material Safety Data Sheets (MSDS) and Technical Data Sheets provided by the suppliers and a literature survey.

A live audit involves the collection and analysis of new data.[64] The new data for this project was obtained from on-site measurements using direct reading instruments, sampling and chemical analysis results of the process, rinse and drag-out tank solutions, and observing the work practices. The new data obtained from the chemical analysis of the rinse tank solutions are used to determine the costs of the wasted raw materials in the

wastewater, entering the sewer. The concentration of the elements which comes from the raw materials in the wastewater is estimated using the concentrations of the elements in the rinse tanks that are discharged into the waste stream. The mass of the elements in the effluent stream that comes for the raw materials can be calculated from the flow rate of the effluent and the concentration of the elements. This can be expressed as a mass or volume of that raw material when the components of the raw material are known. The MSDS sometimes provides the composition of the raw material although some chemical are patented and the chemical composition is not given.

The waste minimisation audit techniques are discussed below.

3.3.1 Scoping Audit

The scoping audit is a technique to help identify potential priority areas for waste minimisation by estimating the potential savings that can be gained through waste minimisation. The data required for a scoping audit are the annual costs and amounts of materials, utilities and waste produced. This information is used in the waste minimisation cost assessment table[64,84] (see Table 3.1).

Each material, utility and waste has a minimum and maximum scope to save percentage allocated to it. These scope to save percentages are published by the United Kingdom Environment Agency and were developed for industries in the United Kingdom.[64] The cost of each input or output stream is multiplied by its respective scope to save percentage. This gives the scope (min) and scope (max) values. The scope (min) is the minimum savings that can be made through a waste minimisation programme and scope (max) is the maximum savings that can be made.[64] These scope to save values are then ranked (in the priority column).This helps to identify the area where the largest savings can be made. The waste minimisation opportunities can then be focused on those areas that stand to achieve the largest financial savings.[64,84]

Table 3.1 Waste Minimisation Cost Assessment Table for a Scoping Audit [64]

Resources and Services	Quantity	Units	Cost/ year	Scope to Save %	Scope (min)	Scope (max)	Priority (1 = Highest)
Materials :							
Raw Materials				1-5			
Cleaning Agents				5-20			
Packaging				10-90			
Utilities :							
Electricity				5-20			
Heat				10-30			
Water				20-80			
Waste :							
Effluent				20-80			
Solid Waste				10-50			
TOTAL							

3.3.2 Mass Balance Analysis

After mapping all stages of the electroplating process, the next step is to identify the amounts of materials, utilities and wastes at each processing stage. All materials, water and energy entering a process exit as either a useful product or waste (see Equation 3.1). A mass balance analysis shows where resources are used and how much is converted to waste rather than becoming useful product.[64]

A mass balance assessment allows the company to track the chemical and water ingredients through the various metal finishing processes. It is based on the simple principle of materials in equal materials out. It also helps determine which components of the process will benefit from the waste minimisation initiatives.[74,85] The mass balance analysis helps show where the waste is generated and identifies the quantity or magnitude of waste by comparing all inputs (raw materials and water) to outputs (products, effluent etc.) from a site, individual departments, processes or unit operations and quantifying the losses.[64] The historical and new data are used to identify the inputs and outputs.[64]

$$\text{Waste} = \text{Inputs} - \text{Outputs} \qquad \textit{Equation 3.1}$$

In this dissertation a water mass balance analysis was conducted on the electroplating line. A water mass balance shows where the water enters and leaves a process and where it is used within the process. The water balance is used to identify and implement waste minimisation opportunities to reduce water use.[86] It also helps to understand and manage water and effluent efficiently, identify the areas with the greatest opportunities for cost savings and detect leaks.[85,86] The simple principle of this analysis is that the amount of water entering the line equals the amount of water leaving the line.[87] The data required for this analysis include water bills, flow rates and operating hours of taps used in the process.[74,87]

3.3.3 True Cost of Waste

Most companies usually underestimate how much waste is costing them; it can be as high as 4% of the annual turnover. The true cost of waste is not limited to the cost of disposal; it also includes the wasted raw materials, energy and labour (see Figure 3.5). This can be up to 5-20 times more than the cost of disposal.[67,85]

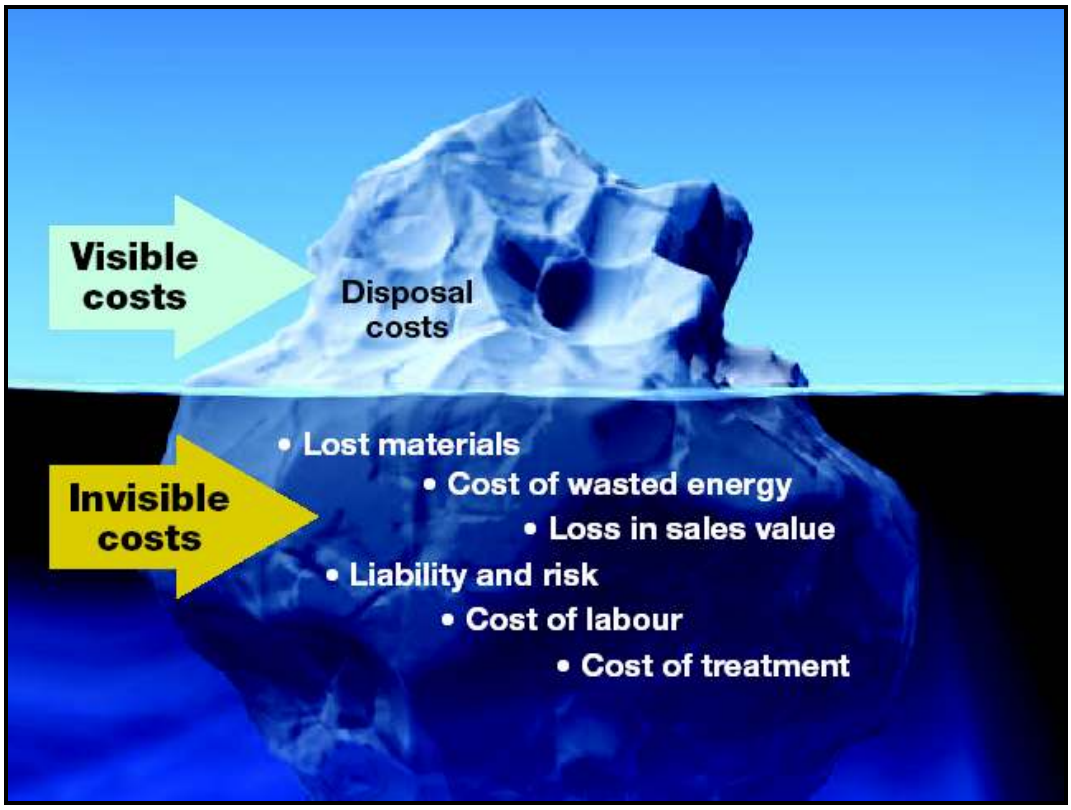


Figure 3.5 Ice berg model of the true cost of waste[85]

As shown in Figure 3.5 the cost of disposal of waste is just the tip of the iceberg, the hidden costs account for the bulk of the cost of waste.

The true cost of waste is the cost of the raw material in the waste added to the cost of disposal. The information required for the calculation of the true-cost of waste includes:[64]

- raw materials costs
- processing costs including effluent treatment, air emissions abatement cost, rework costs
- the effect waste has on capacity by reducing productivity
- costs for monitoring a particular discharge
- environmental liabilities in storing and disposing of waste

The true cost of waste can be calculated using the equations below[64], in terms of the loss of raw materials (e.g. process chemicals) in the effluent stream. These equations were used in this project to estimate the true cost of waste of the effluent stream.

$$\text{Loss of raw material in waste} = \text{Amount of raw material purchased} - \text{Amount of raw material in product}$$

Equation 3.2

$$\text{Cost of raw material in waste} = \text{Loss of raw material in waste} \times \text{Unit cost of raw material}$$

Equation 3.3

$$\text{Raw material cost of waste} = \text{Cost of raw material in waste} + \text{Cost of disposal of raw material in waste}$$

Equation 3.4

3.3.4 Monitoring and Targeting

Monitoring and Targeting is the measurement of the consumption of raw materials and utilities (such as water and energy) as a function of a process variable (usually the production output).[84,88] It is a useful technique for determining waste minimisation opportunities where there is a variable target such as energy or water consumption. Monitoring and Targeting analysis also includes the determination of the performance levels of a company, setting obtainable targets or goals for the consumption of a particular resource, and ongoing monitoring and feedback of progress made.[88] Monitoring and Targeting results are displayed graphically; with the commonly used graphs being trend graphs and XY scatter plots.

The XY scatter plots allow for the comparison of raw material and utility consumption (water and energy) to a relevant production variable (i.e. performance).[64,66,88] Figure 3.6 shows an example of a XY scatter plot, the consumption of water over a particular time period is plotted as a function of the mass of product manufactured over the same time period.[66,88]

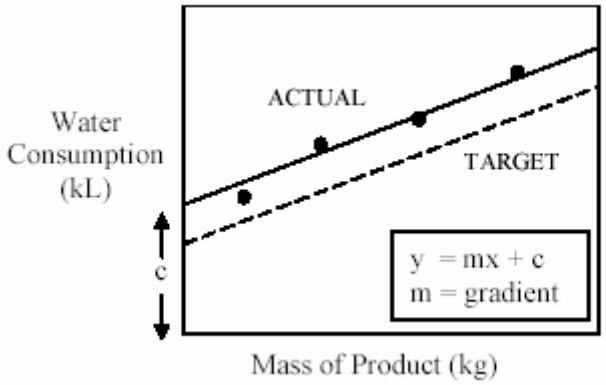


Figure 3.6 XY scatter plot of water consumption as a function of production[88]

From the scatter plot a "best fit" regression line can be added. The three key features represented on the regression line for the process are:[66,84,88,89,90]

- the y-intercept gives the base load of the process i.e. the implied consumption at zero production.
- the slope or gradient gives the direct relationship between production and consumption i.e. the efficiency of the process (which can be assessed from the slope). The smaller the slope the higher the efficiency.
- the scatter of points gives the degree of variability in the consumption. It therefore gives a measure of the level of control exerted over the process.

Determining the reasons for the scatter of points (i.e. low process control) and the large magnitude of the y-intercept (i.e. high base load) and slope (low process efficiency) enables the identification of waste minimisation opportunities for the process.[66,88] Ideally an XY scatter plot should have a y-intercept close to zero (low base load), the scatter of data points should be close to the regression line (good process control) and the line should have a small slope (high process efficiency). This can be achieved through the use of a waste minimisation programme.[84,88]

A target can be set for future production in order to improve the efficiency of the process. The target is included in the XY scatter plot and represents the desired consumption of the resource related to production. The practicality of this target should be verified through the use of a mass balance analysis.[88] The regression line can also be used for targeting. The line can be used as the initial target for the process, with the objective of ensuring all future points on the scatter graph fall on or beneath the target line. This can be viewed as an achievable target since it is based on historical performance, however it is also a challenging target as it implies a performance of better than average.[89]

A trend graph shows the actual material consumption over a period of time. The trend displays the data in a form that enables the comparison between time periods by showing the seasonal variations in raw material and utility consumption. However these graphs show no measure of performance, as they do not take into account fluctuations in the consumption of raw materials due to production output.[66,84,88] A target line can also be included in a trend graph. The target indicates the desired or expected consumption for a process. Waste minimisation opportunities can be identified through the process of attaining this target.[84,88] An example of a trend graph is shown in Figure 3.7.

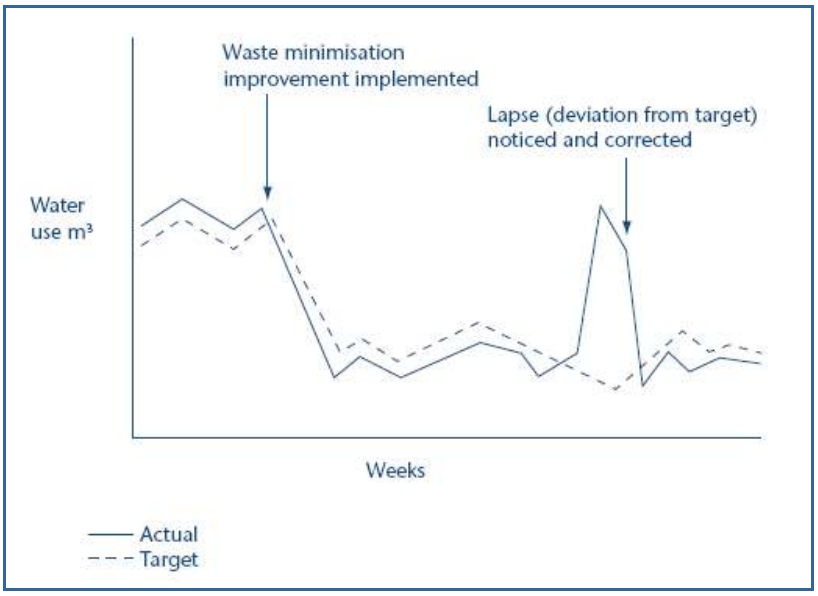


Figure 3.7 Trend graph showing variations in weekly water consumption[64]

Monitoring the amount of water usage is of utmost importance to any metal finishing company. A survey was conducted by Envirowise in the United Kingdom metal finishing industry, on water use. The data was collected and analysed to provide statistical information on resource use and to build an industry profile. The empirical data collected from the metal finishing companies in the United Kingdom was used for Monitoring and Targeting analysis and yielded the water economy diagrams[74,91] (see Figure 3.8). These diagrams show the average water usage as a function of the surface area and mass of workpieces treated. Two target lines were drawn on either side of the average line, one above and one below the average line. This gives rise to four different areas on the graph; each area represents a different category namely best 25%, better than average, worse than average, and worst 25%. Once the water consumption per year (m^3/year) and the surface area or tonnes treated per year is estimated a company can determine the category into which they fall. The water economy diagram gives a means for benchmarking against industry norms. This will enable the company to determine if they are using water efficiently or if there is a need to improve their water usage.

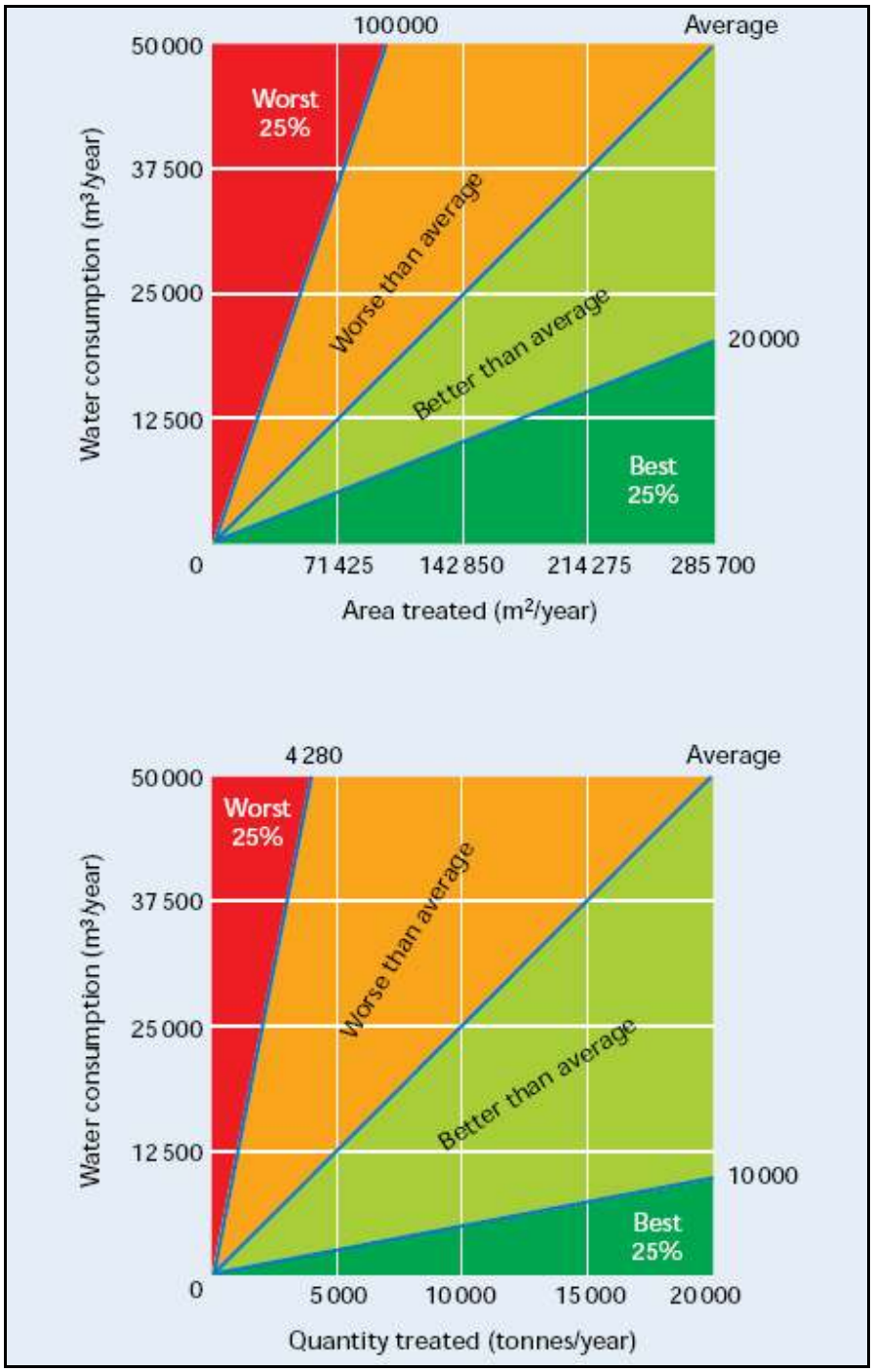


Figure 3.8 Water economy diagram based on Envirowise survey[91]

3.4 Waste Minimisation Options in Electroplating

In the electroplating industry the common areas of waste are excessive water consumption, wastewater and loss of chemicals due to drag-out and spillage. The waste minimisation opportunities for the electroplating industry are described below. These methods are usually low-cost or no-cost approaches to waste minimisation.

3.4.1 Waste Minimisation Options for the Process Baths

The waste minimisation opportunities available for process baths include material substitution, extending the bath life and good house keeping techniques.[83]

Many electroplating processes use toxic chemicals such as Cr(VI) and cyanide in the process baths. Substituting these chemicals with safer non-toxic chemicals can simplify the waste water treatment, reduce treatment costs, eliminate the need to detoxify these wastes and decrease sludge generation.[83] Due to increasing concern over toxic wastes produced by the electroplating and stringent environmental regulations there has been strong research to replace Cr(VI) in the plating industry.[92] Cr(VI) is a proven carcinogen to both humans and animals.[93,94] An alternative to using Cr(VI) in decorative plating is the use of the non-hazardous Cr(III) plating baths.[92,95,96] Recent research has shown that using Cr(III) in certain applications for decorative plating has been successful.[95,97] Chlorinated and non-chlorinated solvents are often used to degrease workpieces in the pre-treatment stages before they are processed. Solvents can be substituted by hot alkaline baths; this allows the baths to be treated on-site and discharged and also produces less sludge than solvent degreasing.[83,98]

Spent process bath solutions are process baths that have become too contaminated to be used for plating and require dumping. This leads to waste generation as the solutions are either treated on-site and disposed of or sent for off-site disposal.[69,83,99] The waste volume and disposal and replacement costs can be minimised by extending the life of the process baths. The methods for extending the life of the process baths include filtration,

monitoring of the bath parameters to ensure they are operating at their optimum and good housekeeping techniques.[83]

Filtration systems remove accumulated solids that reduce the effectiveness of the plating bath operations. Continuous filtration removes contaminants thereby maintaining the bath purity and extending the life of the bath.[83,96,100]

The proper control and monitoring of the bath operating parameters can result in a longer bath life as well as consistent workpiece quality.[83,101] The first step in monitoring the plating baths is to determine the optimum operating parameters (e.g. pH and the metal content) for the process.[101] The next step is to ensure the continuous analysis of the bath parameters, this is essential in determining the proper quantity of chemicals to add to maintain efficient operating parameters.[96,100]

Good house keeping involves keeping the plating areas and plating baths clean and preventing foreign material from entering or remaining in the plating bath. This can prolong the life of the bath. In order to reduce contamination any workpiece that may fall off the rack into the bath should be removed quickly. The operators should also maintain the racks to ensure that they are clean and free of contaminants.[83,96] Another good house keeping technique is using pure anodes, as impurities will contaminate the process baths. Cloth bags can also be used to contain the anodes, thereby preventing insoluble impurities from entering the bath.[83,96]

Another waste minimisation opportunity available for chromium plating baths is the prevention of toxic chromium mists escaping into the air. As well as the loss of chromium from the baths, chromium mists are a health hazard. In Cr(VI) plating baths, approximately 75-85 % of the available power supplied leads to the generation of hydrogen gas.[92] The evolution of hydrogen gas produces a mist of fine water particles with entrained Cr(VI).[96] The release of chromium into the air with the mist is inhibited by forming a physical barrier on top of the plating bath by using mist suppressants. A mist or fume suppressant is a chemical used that forms a barrier on the surface of the plating bath

solution to prevent the mist from escaping into the air. During the plating process the mist suppressant generates a foam blanket and traps the gases between the bath surface and the blanket or within the foam blanket.[96,102]

3.4.2 Waste Minimisation Options for the Rinsing Process

Rinsing is a critical step in the plating process, it prepares the workpiece for subsequent finishing operations, stops chemical reactions, and prevents cross contamination of the subsequent plating tanks.[103] Rinsing accounts for around 95 % of all water used at most metal finishing plants.[74]

The rinsing operation is the primary source of waste generated in the electroplating process.[68,83] Most of the hazardous waste in electroplating operations comes from the wastewater generated from the rinsing process.[103] The rinse water volume and wastewater volume can be reduced by improving the efficiency of the rinsing operations and by measuring and controlling the flow of water to the rinsing systems.

3.4.2.1 Improving rinsing efficiency

Counter current rinsing, spray or fog rinsing and agitation are some of the waste minimisation techniques that decrease water usage and increase the efficiency of the rinsing operations.

Countercurrent rinsing uses a series of connected rinse tanks that rinse the workpiece in sequence. The water flows in the opposite direction of the work flow. Fresh water from the mains enters the final (cleanest) rinse tank and is then conveyed through the other rinse tanks in sequence. The waste rinse water exits the system from the first (dirtiest) rinse tank (see Figure 3.9). The volume of water used is significantly reduced and rinsing is more effective as concentrations of the drag-out chemicals in the rinse tanks are kept low.[74,103] A countercurrent rinse system that uses three rinse tanks (see Figure 3.9) can achieve 95 % reductions in rinse flows and in a two stage system reductions of 90 % are possible.[83,103,105] The use of counter current rinsing is one of the most effective water use minimisation technique available in the electroplating industry.[74]

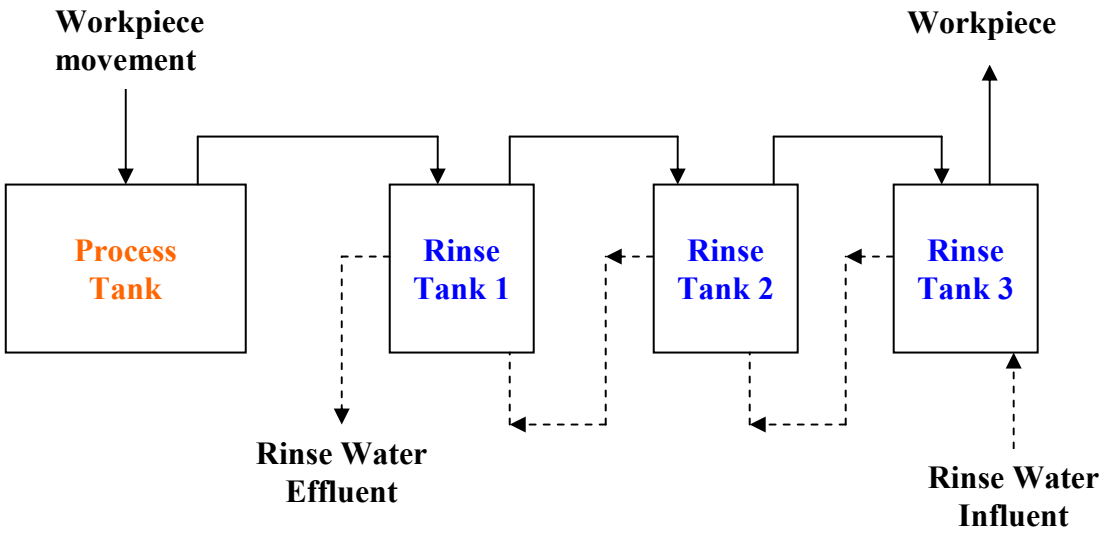


Figure 3.9 A three stage countercurrent rinse system[74,83,104]

Spray and fog rinses above the process baths are effective rinsing techniques that make efficient use of water. These techniques wash drag-out from the workpieces by jetting water over the workpiece. This method also drains off process solution more effectively by reducing the viscosity of the drag-out solution on the workpieces.[75] Spray and fog rinsing are effective over hot process baths as they return the drag-out directly to the process bath, while the flow from the spray replenishes evaporative losses.[74,104]

Agitation in rinse tanks improves the rinsing efficiency by removing the process chemicals with turbulence. This also reduces the time required for rinsing.[98,103,106] The rinse water can be agitated by ultrasonic or mechanical agitation or by pumping air or water into the tanks.[103]

3.4.2.2 Measuring and controlling rinse water flow

Measuring the water use in rinsing helps identify where excessive amounts of water are being used. It can also act as a reminder to employees for the need to reduce water use. The installation of water meters on the process line or on each water inflow point in the process line allows the company to monitor their water usage.[74]

The volume of water passing into continuous flow rinses can be excessive if they are not carefully controlled. Flow restrictors are simple devices that can be used for controlling and limiting the volume of water flowing through a rinse system by limiting the volume of water that can enter the system at the source.[74,75,81,102,103] The equations below (see Equations 3.5 and 3.6) help determine the most efficient rinse water flow rate, for a single stage flowing rinse system (Equation 3.5) and for a counter current rinse system (Equation 3.6).[10,83,102,107,108] Once the appropriate flow rates are determined the flow of water can be controlled by use of flow restrictors. This can result in a significant reduction in water use.[83,103]

$$Q = D\left(\frac{Cp}{Cr}\right) \qquad \textit{Equation 3.5}$$

Q = Rinse flow rate

D = drag-out rate

Cp = chemical concentration in process solution

Cr = concentration in rinse solution

$$Q_N = D\left(\frac{Cp}{Cr}\right)^{\frac{1}{n}} \qquad \textit{Equation 3.6}$$

Q_N = volumetric rate of rinsing for each tank

D = volumetric rate of drag-out

Cp = concentration in process solution

Cr = concentration in final rinse solution

n = number of tanks in series

3.4.2.3 Drag-out Reduction

Drag-out is the term given to the solution that is carried out of the process bath and into the succeeding tanks.[10] Drag-out is the principal source of contamination in rinse water and is a significant cause of chemical loss from plating and other process baths. Drag-out reduction can therefore be a very effective method in reducing waste and conserving water in rinsing operations. Reducing drag-out can also extend the life of the process baths as it will minimise the impurities going into the baths.[75]

The following techniques assist in reducing drag-out and will be discussed below:

- Workpiece withdrawal and drain time
- Workpiece positioning on racks
- Rack maintenance
- Process bath operating conditions
- Drain boards
- Drag-out tanks
- Air knives

Workpiece withdrawal and drain time

The speed at which workpieces are removed from the process bath can affect the drag-out volume. The slower a workpiece is removed from a bath the thinner the film of the process solution that adheres to the workpiece and hence less solution is dragged into the succeeding rinse tanks. Therefore workpieces should be withdrawn slowly from the process baths to minimise drag-out.[83,101,103,106]

By extending the drip time the process solution can be properly drained from the workpieces. Studies have shown that by doubling the drip time from 15 seconds to 30 seconds, the amount of electrolyte returned to the plating solution increased by 50 %.[74,75,104]

Workpiece positioning on racks

The positioning of workpieces on the racks is very important; the workpieces should be positioned so as to allow the solution to drain freely without being trapped in grooves or cavities. Ideally the workpieces should be tilted to allow for better drainage, and workpieces should if possible not be hung directly over one another. The drainage of solution is more efficient when the workpieces are staggered rather than hung directly above one another.[74,75,81,83,101,103]

Rack maintenance

The racks should always be properly maintained. Rack coatings that are loose and have bubbles can lead to the transport of chemicals from the process solutions into the rinse systems.[106] For example it has been observed that chromium may appear in rinse waters some distance from the chromium plating solution due to the solution adhering onto loose rack coatings.[81]

Process bath operating conditions

The chemical concentration of the process bath can affect drag-out, as the chemical content of a solution increases so does its viscosity. An increased viscosity leads to a larger volume of drag-out as well as a higher chemical concentration in the drag-out. Drag-out can be reduced by keeping the chemical concentration of the process baths at the lowest acceptable operating level.[75]

Drain boards

Drain boards can be used between the process and rinse tanks so that it covers the entire space between the two tanks, the board should be sloped allowing the process solution to drain back into the previous bath. This enables the drag-out and drippage to be collected when transferring racks from the process tank to the rinse tank.[74,75,81,101] The use of drain boards is a cost effective technique for reducing chemical consumption and rinse water contamination.[103]

Drag-out tanks

Drag-out tanks are essentially static rinse tanks that operate without a continuous flow of water supply. The drag-out tanks are usually used with plating tanks that operate at higher temperatures. The workpiece is immersed into the drag-out tank after plating and prior to the standard rinsing operations. The chemical concentrations in the drag-out increases as workpieces are immersed into the tank. Therefore the chemical concentration of the solution in these tanks will increase such that it can be used to replenish the plating baths. The addition of the drag-out solution back into the process baths compensates for evaporative losses that occur because of high temperatures.[81,83,103,109]

Air Knives

Electroplaters can use air knives to blow air across the surface of workpieces as they are withdrawn from the process or rinse solutions thereby physically pushing the liquid off the workpieces. This technique returns solution directly to the process bath reclaiming drag-out and reducing the amount of rinse water required to clean the workpiece.[81,83,98,103]

CHAPTER 4

SCOPE AND AIMS

A waste minimisation audit was undertaken on a chromium plating line (CPL) of Howick Metal Products, a local manufacturer of door and window fittings. The CPL is made up of four surface treatment processes, namely cleaning, acid dipping, nickel and chromium plating and neutralizing. Waste minimisation has proven successful for many companies by improving their economic benefits and reducing their environmental impact. This is achieved through reducing the raw material and resource consumption and costs as well as the waste treatment and disposal costs. The increasing awareness and need to protect the environment and our natural resources further increases the importance of waste minimisation. A particular important natural resource for South Africa is water. With warnings of a potential water crisis in the future[110,111], it is imperative to ensure its protection by using water more effectively and avoiding any unnecessary wastage of it.

There are many sources of waste arising during the plating of workpieces, namely:

- Water, chemicals and electricity (for plating) overuse.
- Waste rinse water, spent process solutions, solid waste, airborne particulate and fume production.
- Overuse and wastage of electricity for heating process and rinse solutions and for filtering nickel plating solutions.

This project focuses on the material flows into and out of the chromium plating line. Electricity is a major input to and concern to the electroplating industry. However it is beyond the scope of this project to consider electricity as a potential waste minimisation opportunity here.

There are eight main aims to this project which are listed below:

- To collect accurate quantitative and cost data on material inputs and outputs on the chromium plating line.
- To measure the concentration profile of selected elements within tank solutions on the CPL for a four month period.
- To investigate the relationship between the concentration levels of metals in the rinse water obtained through sampling and chemical analyses and the conductivity and total dissolved solids measurements.
- To establish the extent to which concentration and conductivity data can be used in waste minimisation analysis and whether the concentration results obtained above are a valuable input to a waste audit.
- To compare the results from the application of three waste minimisation techniques on the CPL in order to identify and quantify waste minimisation opportunities. These are:
    1) Mass balance analysis: performed on the water usage
    2) True cost of waste: performed on the chemical wastage
    3) Monitoring and targeting: performed on the water usage
- To compare values obtained for the drag-out rate using chemical analysis with suitable drag-out rates citied in literature.
- To estimate the effluent concentration and compare the results with effluent discharge limits.
- To establish the potential of water as an area for waste minimisation using a water economy diagram.

CHAPTER 5

COMPANY AND PROCESS PROFILE

Howick Metal Products (Pty) Ltd (HMP) was established in 1981. The company is situated in Merrivale, KwaZulu-Natal. It has developed into a major manufacturer of hardware for the building industry and other specialist industrial users. It manufactures door and window fittings.

HMP makes a range of such fittings both in brass and aluminium. These include brass and aluminium hinges, brass window fittings, brass and aluminium door fittings, aluminium door furniture, screws, brass wood screws and stainless steel toilet rollers. They are one of the largest manufacturers of brass hinges in South Africa. The company supplies products to customers locally in South Africa as well as exporting to neighbouring countries in the Southern African region.

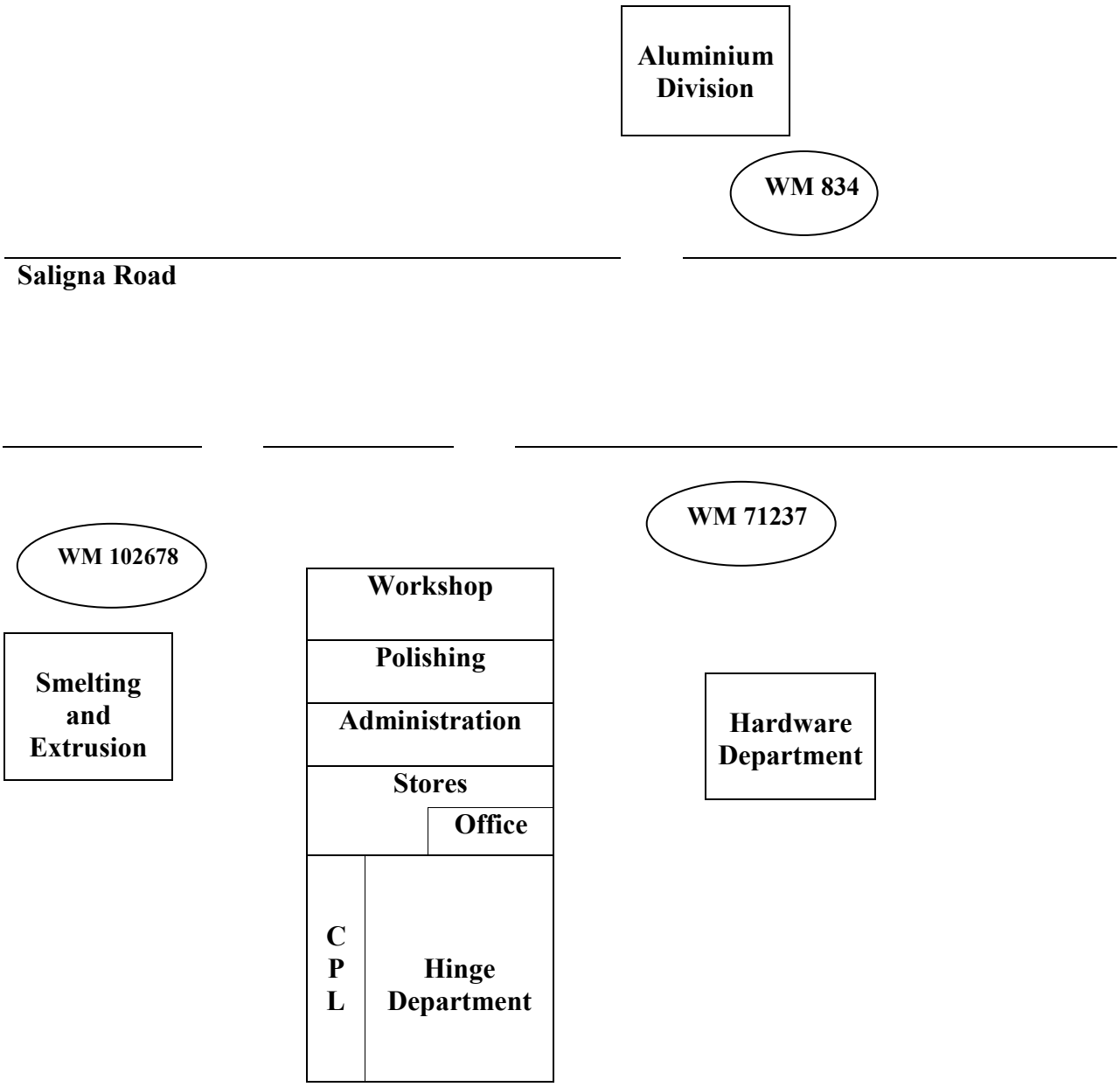
5.1 Company Description

The company is made up of two divisions. These are the Brass and Aluminium Divisions. The Brass Division is made up of smelting and extrusion, hinge department, hardware department, chromium plating line (CPL), polishing, finished goods dispatch, administration and workshop. The smelting and extrusion plant is considered part of the Brass Division, however it has a separate water meter. The Aluminium Division consists of the anodizing, powder coating and finished goods dispatch. The Brass Division will be discussed in Section 5.3 and the Aluminium Division in Section 5. 4.

The company employs approximately 150 people. Working hours are from 6:45 to 15:00, Monday to Friday. There is a 15 minute tea break in the morning from 9:30 to 9:45 and a half hour lunch break at 11:45 to 12:15. This makes a total of 7½ working hours per day. The company operates for 238 days per year. The company closes for all twelve public

holidays per year. They also shut down for a total of three weeks during the Christmas and New Year period.

There are three different Umgeni Municipality water meters, one for the smelting and extrusion plant (102678), one for all other departments in the Brass Division (71237) for example the CPL, hardware, and hinge department and lastly there is one meter for the Anodizing Division (834). The locations of these meters are shown in Figure 5.1.



WM- Umgeni Municipality Water Meter

Figure 5.1 Map of the Company

5.2 Product Description

HMP manufacture their own brass alloys for their workpieces. They make two different types of brass, namely, 202 and 218 (see Section 5.3.1 for composition). The difference between the two is that one is softer (218) and the other is harder (202). The softer brass (218) is easier to machine (punching and bending), and this is used for all light duty workpieces. The harder brass (202) is used for the heavy duty products. Window and door hinges and bolts are the major product manufactured and plated by the company. Figures 5.2 to 5.6 show 5 of the workpieces manufactured by the company.

Table 5.1 Company codes and names of the brass workpieces

Code	Work piece	Code	Work piece
H006	Canopy hinge	H100	Barrel bolt
H007	Canopy hinge	H101	Barrel bolt
H012	Butt hinge	H102	Barrel bolt
I014	Butt hinge	H104	Barrel bolt
I016	Butt hinge	H105/12	Barrel bolt
I020	Butt hinge	H105/6	Barrel bolt
H021	Butt hinge	H103	Neck bolt
I022	Butt hinge	H106/6	Neck bolt
H023	Butt hinge	H107	Neck bolt
H028	Butt hinge	H108	Neck bolt
H036	Washered butt hinge	H108	Neck bolt
I048	Sinkless hinge	H110	Neck bolt
H049	Sinkless hinge	H429	Lever flush bolt
H051	Sinkless hinge	H420	Lever flush bolt
H064	Window hinge	H122	Escutcheon
H082	Parliament hinge	H121	Escutcheon
H083	Parliament hinge	H201/1	Fanlight stays
H084	Parliament hinge	H080	Sash fastener catch
H085	Parliament hinge	H081	Sash window lift
H070	Projection hinge	H076	Heavy duty spring clip
H073	Projection hinge	H315	Casement handles
H053	Hasp & Staple	H316	Casement handles
H054	Hasp & Staple	H055	Hasp & Staple

Figure 5.2 Canopy hinges

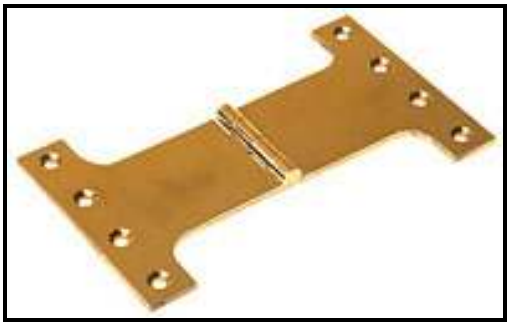


Figure 5.3 Parliament hinge[112]

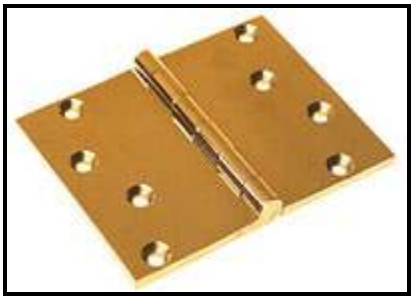


Figure 5.4 Projection hinge[113]

Figure 5.5 Barrel bolt[114]

Figure 5.6 Neck bolt[115]

5.3 Brass Division

The Brass Division consists of 8 departments and 85 workers in total. There are 13 showers and 19 toilets located in this division. A brief description of the 8 departments is given below.

5.3.1 Smelting and Extrusion

This plant is located in a dedicated building in front of the hinge and hardware department. The brass alloys that the company uses to manufacture its workpieces are made on-site in this department. The brass alloy is made from Cu, Al, Zn and Pb. As mentioned earlier in Section 5.2 the company makes two types of brass alloys 202 and 218. The composition of the brass alloys is given in Table 5.2. Both these alloys contain less than 0.3 % impurities (iron and tin).

Table 5.2 Composition of the brass alloys

Brass alloy	Constituent (%)			
	Cu	**Zn**	**Pb**	**Al**
202	57	40.7	2	0.3
218	58	40.5	1.5	-

5.3.2 Hinge department

The hinge department is the place where the manufacturing of all the hinge products occurs. This department receives the extruded brass from the smelting and extrusion plant. The extruded brass is received in different sizes, termed sections. These sections then undergo several processes to get the final hinge product.

5.3.3 Hardware Department

The hardware department is responsible for the manufacture of all other brass products excluding the hinges, for example barrel bolts, neck bolts, fanlight stays and casement handles. They use similar processes to the hinge department.

5.3.4 Polishing

Polishing is a mechanical technique used to produce a smooth surface, usually with high reflectivity. Wokpieces that do not require chromium plating are simply polished. Polishing produces a high gloss finish to the product.

5.3.5 Chromium Plating Line

Workpieces that are electroplated will undergo either satin or bright chromium plating. The chromium plating line (CPL) will be discussed in detail in Section 5.5

5.3.6 Finished Goods Dispatch

This department contains the product and customer information regarding the destination of the final products. The finished products are brought here to be sent out to the customers.

5.3.7 Administration

This department carries out the usual administration duties including project planning, sales, accounts and requisitions.

5.3.8 Workshop

The workshop is responsible for the electrical and mechanical maintenance of the whole plant. If tools need to be sharpened, or machines fixed, they are sent to the workshop for repairs.

5.4 Aluminium Division

The Aluminium Division is situated on the opposite side of the road to the Brass Division. The Aluminium Division purchases their raw materials from Euro Steel and solution chemicals for the anodising line from Artek (KZN). This division employs approximately 40 workers. They make the same products as the Brass Division. However the hinge and hardware manufacturing is carried out in one department. The Aluminium Division is a different section and their products do not undergo electroplating on the CPL; therefore, only a brief description is given as there was no need to focus on this division for the waste minimisation audit.

5.5 Process Description for the Chromium Plating Line

The chemical supplier for the process solutions used on the CPL is currently Artek (KZN). Chemical stock from the previous supplier, Orlik, is still being used on the line for example Orprep HP 100 and Orprep HP 16 in Tanks 1 and 3 respectively (see Figure 5.8). When these are finished Artek chemicals will be used to top up the solutions for example SK 40 and EL 80 in Tanks 1 and 3 respectively.

The volume of the tanks, the operating conditions during plating and the specified concentrations of the chemicals for the process solutions and their chemical compositions are given in Table 5.3. The entry in the fourth column of Table 5.3 shows the temperature (°C) of the solution, the amperage (A) going through the solution and the voltage (V) applied to the solution. The composition of the chemicals used on the CPL were obtained through personnel communication with the chemical supplier from Artek and from the material safety data sheets (MSDS)[116-121], however these sheets are often vague and only list the main ingredients.

The chemical supplier from Artek takes samples from the seven process solutions (tanks 1, 3, 7, 10, 11, 15 and 17) see Figure 5.8, once a month for analysis. The line operators top up the solutions based on the analysis results from the chemical supplier. These results are faxed to the company by the chemical supplier. They contain the optimum concentrations for running the solutions and the additions which have to be made to restore the measured level to the specified concentration. This will be referred to as the Analysis Report. However no formal record of this is kept apart from the addition quantities indicated on the chemical analysis report. Some chemicals are added on a needs basis, this includes for example the fume suppressant, Fumetrol 140 in the chromium plating solution and sodium metabisulfite in the neutralizer tank.

The layout of the CPL, showing the tank arrangement, water influent and effluent and location of the mains taps is shown in Figure 5.8. The CPL consists of 21 tanks. Seven tanks are process solutions which include the cleaning and plating tanks, and the other fourteen are rinse tanks. The process tanks comprise of three cleaning tanks (1, 3 and 7),

two nickel plating tanks (10 and 11), a chromium plating solution (15) and a neutralizing tank (17) which reduces Cr(VI) to Cr(III) and neutralizes any acid remaining on the workpieces. The rinse tanks consist of the cleaning rinse tanks (2, 4, 5, 6, 8, and 9), the nickel rinse tanks (12-14), as well as the nickel drag-out tanks (20 and 21), the chromium drag-out tank (16), neutralizer rinse (18) and hot water rinse (19). All tanks except for the nickel drag-out tanks are arranged sequentially alongside one wall of the plating shop. The nickel drag-out tanks are placed opposite the nickel plating tanks. The workpieces are either dipped in the satin or bright nickel tank (10 or 11 respectively) followed by immersion into the corresponding static drag-out tank (20 or 21). The jig is then rinsed in the nickel countercurrent rinse tanks (12-14).

Table 5.3 The volume, operating conditions, specified concentrations and chemical composition of chemicals used for the tanks in the CPL

k No.	Tank	Volume (L)	Operating Conditions	Specified Concentration		Chemical Composition
				Ingredient	g/L	
	Soak Cleaner	95	64°C, 8.5 A	Orprep HP 100 (SK40)	75	sodium silicate (Na_2SiO_3) sodium hydroxide (NaOH) sodium carbonate (Na_2CO_3)
2	Soak Cleaner Flowing Rinse	100				
3	Electrocleaner	100	3.5V, 15 A, 5.6°C	Orprep HP 16 (EL 80)	50	sodium hydroxide (NaOH)
& 6	Electrocleaner Countercurrent Rinse	120				
7	Galtin 140	180		Galtin 140 (dry acid salts)	22	Sodium hydrogen sulfate ($NaHSO_4$) Sodium hydrogen fluoride ($NaHF_2$)
t 9	Galtin Countercurrent Rinse	130				
0	Satin Nickel	550	58°C, 5.8V	$NiSO_4.6H_2O$ $NiCl_2$ Boric acid Magnum 821 Leveller	300 65 45 6 30	 Patented Patented
1	Bright Nickel	710	59°C, 5.8V	$NiSO_4.6H_2O$ $NiCl_2$ Boric acid Magnum 821 Leveller Magnum 898	300 65 45 6 30 -	 Patented Patented Patented
&14	Nickel Countercurrent Rinse	110				
5	Chromium Plating	340	47°C, 5.5V,0.28kA	Lumina 34 (Chromic acid) Sulfuric acid Fumetrol 140	300 - -	Patented Chromic acid (CrO_3) and fluor based mixed catalyst system H_2SO_4 Patented
6	Chromium Drag-out	190				
7	Neutralizer	190		Sodium metabisulfite	-	$Na_2S_2O_5$
8	Neutralizer Flowing Rinse	88				
9	Hot Water Static Rinse	200	54°C			
0	Satin Nickel Drag-out	190				
1	Bright Nickel Drag-out	230				

The workpieces are wired onto the jig frames with copper wire for cleaning and plating. The workpieces are wired onto the jigs by hand (see Figure 5.7). The jigs are manually moved from one tank solution to another down the line. Normally two operators work in the chromium plating shop. A timer system is used for the soak cleaner (Tank 1) and nickel (Tank 10 and 11) and chromium (Tank 15) plating tanks. The time when the workpiece should be withdrawn from the solution is indicated by a red light coming on above the tank.

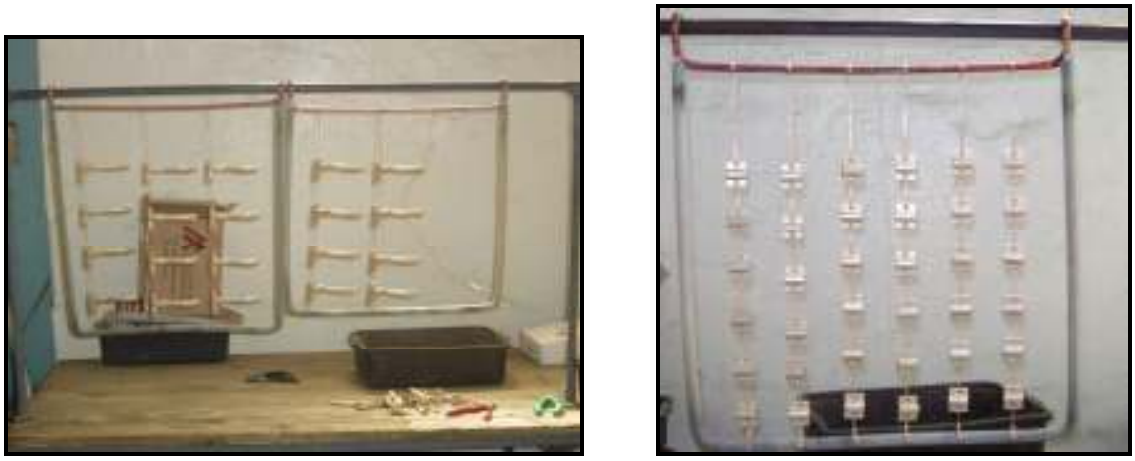


Figure 5.7 The workpieces are wired onto the jig frames with copper wire

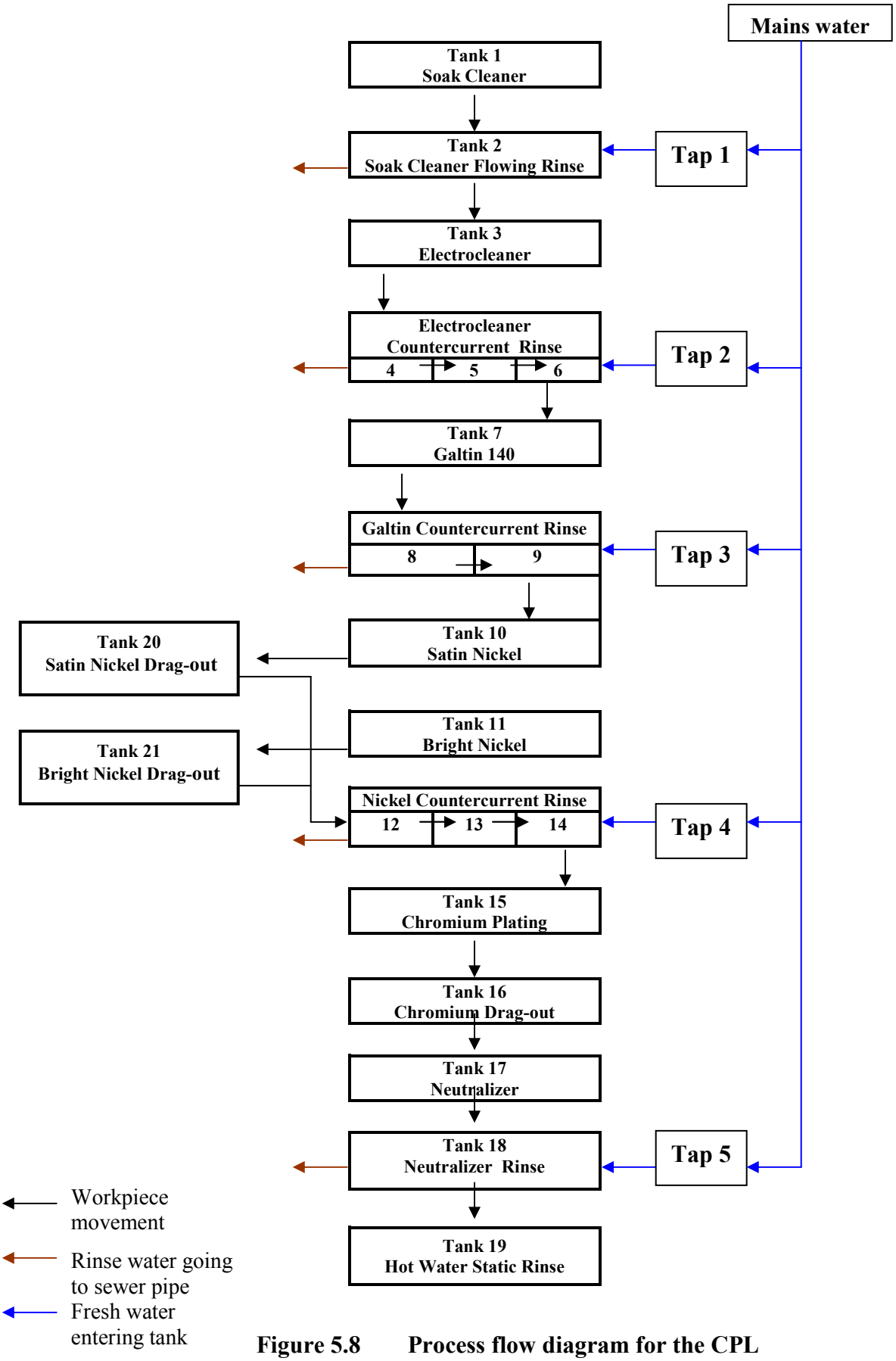


Figure 5.8 Process flow diagram for the CPL

5.5.1 Process Solutions on the CPL

There are three pre-treatment tanks the workpieces go through before the plating tanks. The first two process tanks are an alkaline cleaning system. The first cleaner (Tank 1) is a hot, heavy duty soak cleaner, used to remove grease and oils. The soak cleaner used is Orprep HP 100, its chemical composition is sodium silicate (Na_2SiO_3), sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3). The increased temperature improves the cleaning efficiency of the soak cleaner. The second cleaner (Tank 2) is an anodic alkaline electrocleaner, the chemical used is Orprep HP 16. Its main ingredient is sodium hydroxide (NaOH). The heated electrocleaner is used to remove any dirt remaining on the workpieces after soak cleaning. The workpieces are immersed in each tank for 10 minutes. The third treatment tank (Tank 3) is an acid dip. The chemical used to make up this system is Galtin 140. Galtin 140 is a mixture of sodium hydrogen sulfate ($NaHSO_4$) and sodium hydrogen fluoride ($NaHF_2$). This tank is used to remove any oxide or scale on the workpiece and it also activates (etches) the surface of the workpiece before plating. The chemicals used in Tanks 1, 3 and 7 and their specified concentrations are given Table 5.3.

After the workpieces have been treated with the pre-plating solutions (Tanks 1, 3 and 7) they are ready for the plating tanks. The workpieces are first dipped into the appropriate nickel solution (Tank 10 or 11). The satin nickel solution (Tank 10) is used to provide a matt finish to the chromium plated workpieces. The constituents of the nickel solutions and the operating conditions are shown in Table 5.3. One of the ingredients in these tanks Magnum 821 is a two part system which functions as a brightener as well as a stress reliever. The bright nickel bath (Tank 11) produces a shiny more lustrous finish to the workpieces. The bright nickel plating bath has an additional brightener and leveller, Magnum 898. However the optimum concentration of Magnum 898 used is not given on the Analysis Reports. The workpieces are immersed into the nickel baths for 10 minutes. After nickel plating the workpieces are dipped into the corresponding static drag-out tank (Tank 20 or 21). The nickel baths are topped up with solution from these drag-out tanks. Approximately 15 L of drag-out is used to top up the plating baths on a daily basis.

Soluble pure nickel anodes are used in the nickel plating tanks and they are contained in fabric bags (see Figure 5.9).

Figure 5.9 Fabric bags used to contain the nickel anodes

The chromium plating bath (Tank 15) is made up of Lumina 34. This is a mixed catalyst system that contains chromic acid, a system that has been specifically developed for decorative chromium plating. The composition of the mixed catalyst system is a trade secret. The workpieces are immersed in the tank for 2 minutes. Immediately after chromium plating the workpieces are dipped in the chromium drag-out tank (Tank 16). The chromium bath is topped up daily with approximately 15 L of solution from the drag-out tank. Insoluble antimonial lead anodes are used in the chromium plating tank.

The post-plating tank which is the Chrome Neutralizer tank (Tank 17), is the last process solution on the CPL. This tank is responsible for converting Cr(VI) to Cr(III) using sodium metabisulfite (see Equation 5.1). This tank is not analysed by the chemical supplier, chemical additions are made as they are required by the line operators. The operators use the colour of the neutralizer solution as an indication of whether an addition is required. The solution should be a green colour, if the colour is dull or changing then an addition of sodium metabisulfite is made into the tank. Workpieces are suspended in this tank for 10 minutes.

$$2Cr_2O_7^{2-}(aq) + 3S_2O_5^{2-}(aq) + 10H^+(aq) \longrightarrow 4Cr^{3+}(aq) + 6SO_4^{2-}(aq) + 5H_2O(l)$$

Equation 5.1

5.5.2 Rinsing on the CPL

The line has five taps that can be individually set to supply water to the rinse tanks. The taps are controlled by one main switch, which opens or closes water supply. The flow rates are controlled by the line operators. There is no water meter connected to the CPL.

The CPL has 10 flowing rinse tanks, 1 static rinse tank and 3 drag-out tanks (see Figure 5.8). The flowing rinse tanks are made up of the 3 countercurrent rinse systems (Tanks 4-6, Tanks 8-9 and Tanks 12-14) and 2 single flowing rinse tanks (Tanks 2 and 18). For the countercurrent rinses the water inlet is through the last tank in the series (i.e. Tanks 6, 9 and 14) and the outlet is through the first tank (i.e. Tanks 4, 8 and 12).

After the workpieces are treated with the process solutions they are rinsed off in the corresponding rinse tanks. The chromium and nickel plating baths have drag-out tanks (Tanks 16, 20 and 21), workpieces are immersed in these tanks for 1 minute. There is also a countercurrent rinse system consisting of 3 tanks for the nickel baths as well as for the electrocleaner (Tanks 4-6). Workpieces are rinsed in these tanks for 3 minutes. Nickel rinsing therefore involves the workpieces being dipped into the appropriate drag-out tank (Tank 20 or 21), followed by rinsing in the countercurrent system (Tanks 12-14). The Galtin tank also has a countercurrent rinse system comprising of 2 tanks (Tanks 8 and 9), workpieces are immersed in these tanks for 2 minutes. The soak cleaner and neutralizer have a single stage flowing rinse system, workpieces are dipped in these tanks for 1 minute. The last rinse tank (Tank 19) is a static hot water rinse and is there is no inflow or outflow of water. This rinse is used to remove any chemicals still present on the workpieces.

The effluent rinse water leaving rinse Tanks 2, 4, 6, 8, 12 and 18 collect in a gutter and are discharged directly into the sewer pipe.

CHAPTER 6

MONITORING METHODOLOGY

The waste minimisation audit was carried out in order to collect and analyse data on the composition, flow rate and cost of the process and waste streams of the CPL. This was undertaken to identify the sources and levels of waste in the process and their expense to the company. Further data were collected in order to estimate the water usage on the CPL. This will have important consequences for the company which is in the process of planning a waste water treatment plant. The data collected falls into one of two types, namely existing (historical) and new (current or live) data. The method of collections and reasons behind collection of specific data are given in Table 6.1.

Table 6.1 Data collected for the waste minimisation audit

Data	Data and data collection method
Existing	Consultation • of factory production records on a weekly basis • of chemical supplier's analysis reports on monthly basis • of Umgeni municipality tax invoices (water bills) one to three monthly basis • with CPL operators and supervisors on a weekly basis • with chemical suppliers on appointment
New	• Elemental composition of solutions on the CPL by sampling and laboratory chemical analyses • Generic solution composition by direct reading instrumental and gravimetric analyses • Estimating water usage on the CPL by taking flow rate measurements • Estimating surface areas of the workpieces gone through the line during the monitoring period • Observing work practices and process operations

The audit took place between 13/02/07 to 19/06/07. This makes a total of 85 days and is called the monitoring period. There was however a two week period from the 24/04 to 7/05 when no monitoring was conducted. This was due to a public holiday falling on the Tuesday, the sampling day. Table 6.2 describes how the monitoring period is broken down into seventeen individual sample periods. Each visit date represents a site visit to the factory to collect information and samples and the sample period (SP) is the time

period from the site visit (and sampling) to the day before the next site visit. Thus samples were only taken at the beginning of each "sample period".

Table 6.2 On-site visit date and sample periods with their corresponding dates

Visit date (sampling date)	Sample period	Sample period duration
13/02	1	13/02 to 19/02
20/02	2	20/02 to 26/02
27/02	3	27/02 to 5/03
6/03	4	6/03 to 12/03
13/03	5	13/03 to 19/03
20/03	6	20/03 to 26/03
27/03	7	27/03 to 2/04
3/04	8	3/04 to 10/04
11/04	9	11/04 to 16/04
17/04	10	17/04 to 23/04
24/04	11	24/04 to 7/05
8/05	12	8/05 to 14/05
15/05	13	15/05 to 21/05
22/05	14	22/05 to 28/05
29/05	15	29/05 to 4/06
5/06	16	5/06 to 11/06
12/06	17	12/06 to 18/06
19/06		

Collection of existing data are discussed in Section 6.1. Collection of new data is presented from Section 6.2 onwards. The new data presented in Section 6.2 does not involve sampling or chemical analysis. Section 6.3 describes sampling procedures used while Sections 6.4 and 6.5 provide new data from chemical analysis and gravimetric analysis respectively. In Section 6.6 the procedure used to obtain the results from direct reading instruments is presented.

6.1 Collection of Existing Data

A print out of the number and type of each workpiece treated on the CPL was obtained from the production foreman of the Brass Division at every site visit. During the monitoring period four Analysis Reports were supplied to the company from the chemical supplier. A method was instituted to attempt to get the line operators to record any chemical additions made to the tank solutions and any dumping of the rinse solutions to the drain. A calendar was pinned to the wall in the CPL. The operators were shown how to record on the calender when and how much chemical additions were made to the line. This however was only partially successful as the line operators recorded certain occasions when chemical additions were made, but did not record the quantity of chemicals used. Also according to the Analysis Reports certain chemical additions were required, but these were not documented by the operators and no dumping dates were recorded during the full monitoring period.

The company occupies three different sites. The mains water supply to each of these sites is metered. Therefore three water bills had to be obtained from the company.

Usually in such waste minimisation studies data on purchased raw materials is collected from the procurement department. These raw materials are held in the store and raw material requisitions are made by the plating plant and drawn from the store. However this case was anomalous. During the monitoring period old stock from the previous supplier was being used up in the CPL. The new supplier was servicing the CPL. They were carrying out analysis of the process solutions and recommending the chemical additions which had to be made. However they were not yet selling chemicals to the company for use on the CPL. Therefore a proper scoping audit was not possible as the company did not purchase any raw materials and no records were kept of the chemicals used and the amount of chemicals still in stock for the CPL during the full monitoring period.

6.2 Collection of New Data not requiring Chemical Analysis

The new data collected on-site that did not require chemical analysis were the measurement of tank dimensions, determination of incoming water flow rates and measurements of the workpiece dimensions.

The measurements of the tanks (see Table 6.3) were done in order to calculate the volume of the solutions. The height was taken from the bottom of the tank to the solution surface (therefore the volume will reflect the volume of the solution). For Tanks 7, 10 and 11 the volumes were already recorded on the front of the tank, therefore there was no need to measure the dimensions. These volumes were used to perform the mass balance analysis on the water used on the CPL.

Table 6.3 Tank dimensions and volumes

Tank	Length (m)	Breadth (m)	Height (m)	Volume (m^3)
1	0.6	0.3	0.53	0.095
2	0.595	0.3	0.56	0.10
3	0.6	0.29	0.57	0.10
4 -6	0.7	0.295	0.595	0.12
7	Volume given on tank			0.18
8-9	0.72	0.291	0.60	0.13
10	Volume given on tank			0.55
11	Volume given on tank			0.71
12-14	0.69	0.285	0.57	0.11
15	0.99	0.58	0.60	0.34
16	0.60	0.52	0.60	0.19
17	0.605	0.53	0.60	0.19
18	0.545	0.28	0.575	0.088
19	0.67	0.48	0.62	0.20
20	0.61	0.535	0.585	0.19
21	0.64	0.605	0.59	0.23

The flow rates of the incoming mains water into five flowing rinse systems (Tanks 2, 6, 9, 14 and 18) was measured at the taps connecting the water supply pipe into the pipe at the bottom of the cleanest rinse solution of the system. There was a funnel at the top of

the pipe which is attached to the bottom of the rinse tank. The water supply tap rested in this funnel. During the measurement the tap was lifted out of the funnel in order to make these measurements. The flow rates were measured using a 1000 mL beaker and a digital stopwatch. The process involved timing how long it took to fill the beaker to a specific volume with water from the tap. Results were collected in triplicate. The average of the three readings was taken for use in calculations. The flow rate was calculated in L/min.

The company does not have any records or blue prints for the surface area of the workpieces. The surface areas were calculated by using the workpiece dimensions. The dimensions were measured using a digital vernier caliper (MIB,Germany) and a tape measure. A formula for calculating the surface area was derived for each workpiece and used together with the dimensional information to estimate the surface area.

6.3 Sampling Strategy used for Collection of New Data requiring Laboratory and Direct Reading Instrumental Analyses

Sampling was conducted on a weekly basis every Tuesday from the 13/02/07 to 19/06/07 as shown in Table 6.2. Samples for the process and rinse solutions on the CPL were taken for laboratory analysis of their elemental composition (see Section 6.4), Total Dissolved Solids (TDS), Suspended Solids (SS), conductivity and pH.

Samples from process and rinse tanks were collected and stored in high density polyethylene (HDPE) bottles. The bottles were first thoroughly cleaned before use. They were first washed with soap and tap water, then washed with 2M HCl and rinsed again with tap water. Lastly they were rinsed with distilled water and left to air dry. Once dry the bottles were labeled. Two samples were collected, one for elemental analysis using 250 mL HDPE bottles and the second sample collected in a 500 mL HDPE bottle was for TDS and SS analysis. Collection of samples for elemental analysis began from the start of the monitoring period (13/02) whereas collection for TDS and SS samples started on the 20/03. A total of 630 samples were taken from the 21 tanks on the CPL during the full monitoring period.

When sampling, the bottles were held at the base and its mouth was gently plunged down into the solution to avoid any surface scum from entering the bottle. The samples were taken from the middle of the tank with the bottle pointing slightly upwards to allow air to escape and the bottle to fill properly. Once filled the bottles were securely closed with the cap. The samples were stored in a cooler box for transportation to the laboratory. In the laboratory the rinse solutions were stored in a refrigerator and the process solutions were kept in an icebox until analyses was performed. The samples were used for elemental analysis, conductivity, pH and gravimetric analysis.

6.4 Chemical analysis of samples using the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

ICP-OES was employed for the determination of eleven elements (Cr, Ni, Na, S, B, P, Si, Fe, Zn, Cu and Pb) present in the process and rinse solutions of the CPL. ICP-OES was used for this analysis due to its ability to rapidly analyse several elements simultaneously and its low detection limits. It also offers the advantage of low chemical interference.[122] In Section 6.4.1 a description of how the instrument works is given while Sections 6.4.2. and 6.4.3 explains how the standards and samples are prepared for analysis.

6.4.1 Principles of the ICP-OES

A plasma is a conducting gaseous mixture containing a significant concentration of cations and electrons. In the argon plasma employed for emission analysis, the argon ions and electrons are the principal conducting species. Argon ions formed in the plasma are capable of absorbing sufficient power from the ICP source to maintain the temperature at a level at which further ionization sustains the plasma indefinitely.[122, 123]

The liquid sample is converted to aerosol or mist by a device termed a nebulizer (see Figure 6.1). The nebulization step is one of the vital steps in the ICP-OES. There are two types of nebulizers used with the ICP-OES, namely a pneumatic nebulizer and an

ultrasonic nebulizer. The concentric nebulizer is the most commonly used pneumatic nebulizer and the nebulizer used during this work. With concentric nebulizers, the sample solution is pumped into a capillary tube by a peristaltic pump. Argon gas flows past the end of the capillary converting the liquid sample into an aerosol. The high speed argon gas combined with the low pressure breaks up the liquid sample into aerosol. Concentric pneumatic nebulizers have excellent sensitivity and stability. [123]

After the sample aerosol is formed by the nebulizer, it has to be carried to the torch so that it can be fed to the plasma discharge. Only fine droplets in the aerosol can be effectively desolvated, vapourized, atomized, ionized and excited in the plasma, therefore large droplets have to be removed from the aerosol. A device called the spray chamber which is situated between the nebulizer and the torch serves this function. The spray chamber allows droplets with diameters of approximately 10 μm or smaller to pass to the plasma.[123]

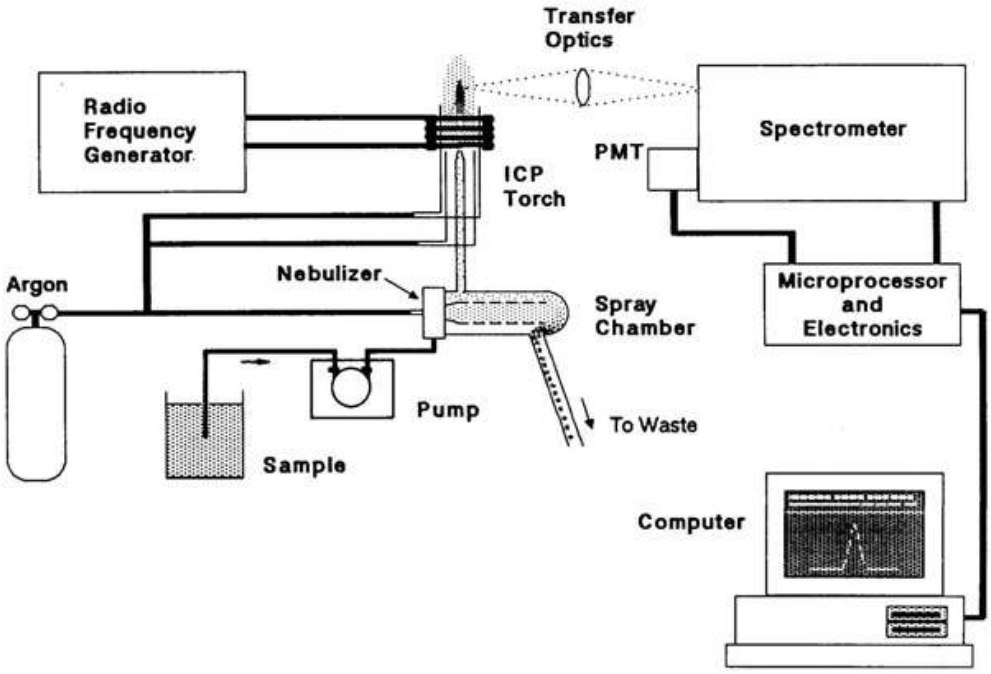


Figure 6.1 The various components of the ICP-OES [124]

The qualitative and quantitative information about the sample is obtained from the light or radiation emitted by the excited atoms and ions. The excited species in the plasma emit light at more than one wavelength, therefore the emission from the plasma discharge is referred to as polychromatic. Polychromatic radiation has to be sorted into individual wavelengths so that the emission from each atom can be identified and quantified without interferences or overlaps from emission at adjacent wavelengths. The separation of light according to their wavelengths is achieved using a monochromator, which is used to measure light one wavelength at a time, or a polychromator, which can measure light at more than one wavelength simultaneously. A polychromator was used in this work. After the separation of light, the detection of the light is performed using a photosensitive device, previously a photomultiplier tube (PMT) was used, however now more improved devices such as a photodiode array (PDA), charge coupled device (CCD) and charge injection device (CID) are used. [123] The ICP-OES used in this study is equipped with a CCD which enables simultaneous detection of all wavelengths.

A major advantage of the ICP-OES is its wide elemental coverage. A second advantage of the ICP-OES is its wide linear calibration range, usually four to nine orders of magnitudes (the upper quantitative limit of an element can be 10^4-10^9 times the detection limit of a particular emission line). A third advantage of the ICP-OES is the simultaneous determination of many elements in the same analytical run. The ICP-OES also experiences the fewest and least severe interferences found in other commonly used techniques for example atomic absorption spectroscopy. The hot plasma is mainly responsible for overcoming the chemical interferences. [123]

The ICP-OES operating details used to process the samples is shown in Table 6.4 and the wavelengths used for the elements are given in Table 6.5. Certain elements (P, Si, Cu, Fe and Pb) were detected using more than one wavelength. The instrument has the ability of measuring the elements using multiple wavelengths which enables the validity of the results to be checked.

Table 6.4 ICP-OES specifications and operating conditions

Parameter	
Instrument	Varian 720-ES
Nebulizer	Pneumatic
Power	1.00 kW
Plasma Argon flow	15.0 L/min
Auxiliary Argon flow	1.50 L/min
Nebulizer flow	0.75 L/min
Pump rate	15 rpm

Table 6.5 Selected wavelengths used on the ICP-OES

Element	Wavelength (nm)
Cr	267.716
Ni	231.604
Na	568.821
S	181.972
B	249.772
P	177.434 & 213.618
Si	251.432& 288.158
Fe	238.204 & 259.940
Zn	206.200
Cu	217.895 & 327.395
Pb	220.353 & 405.781

6.4.2 Preparation of Standards

For the ICP-OES analysis, two sets of standards were prepared for elemental determination. The first set of standards (Set A), Table 6.7, was prepared to accommodate the higher concentration of elements found in the sample solutions. The second set of standards (Set B), Table 6.9, was of lower concentrations, to cover the low concentration range in certain rinse samples. The calibration standards were prepared from a mixed stock standard solution containing all elements required for analysis. All the standards were prepared using ultra pure water. The mixed stock solution was prepared from 1000 mg/L ICP-OES standard solutions purchased from Fluka. The 1000 mg/L Cr stock solution was prepared using anhydrous $K_2Cr_2O_7$ (puriss. 99%) supplied by Riedel-de Haën. This was dried overnight in an oven set at 105°C and thereafter cooled in a desiccator.

Table 6.6 Preparation of mixed stock solution (mg/L) from 1000 mg/L standard solutions

Element	Purchased Solution Conc.	Mixed Solution Conc.
Cr	1000	200
Ni	1000	200
Na	1000	100
S	1000	100
B	1000	20
P	1000	8
Pb	1000	8
Si	1000	8
Fe	1000	8
Cu	1000	8
Zn	1000	8

Table 6.7 Concentration of standard Set A used for ICP-OES analysis

Element	Concentration (mg/L)				
	Std 1	Std 2	Std 3	Std 4	Std 5
Cr	12.5	25	50	100	200
Ni	12.5	25	50	100	200
Na	6.25	12.5	25	50	100
S	6.25	12.5	25	50	100
B	1.25	2.5	5	10	20
P	0.5	1	2	4	8
Pb	0.5	1	2	4	8
Si	0.5	1	2	4	8
Fe	0.5	1	2	4	8
Cu	0.5	1	2	4	8
Zn	0.5	1	2	4	8

Table 6.8 Preparation of 100 mg/L mixed stock solution from 1000 mg/L standard solutions

Element	Purchased Solution Conc.	Mixed Solution Conc.
Cr	1000	100
Ni	1000	100
Na	1000	100
S	1000	100
B	1000	100
P	1000	100
Pb	1000	100
Si	1000	100
Fe	1000	100
Cu	1000	100
Zn	1000	100

Table 6.9 Concentration of standard Set B used for ICP-OES analysis

Element	Concentration (mg/L)					
	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6
Cr	0.01	0.05	0.2	1	5	25
Ni	0.01	0.05	0.2	1	5	25
Na	0.01	0.05	0.2	1	5	25
S	0.01	0.05	0.2	1	5	25
B	0.01	0.05	0.2	1	5	25
P	0.01	0.05	0.2	1	5	25
Pb	0.01	0.05	0.2	1	5	25
Si	0.01	0.05	0.2	1	5	25
Fe	0.01	0.05	0.2	1	5	25
Cu	0.01	0.05	0.2	1	5	25
Zn	0.01	0.05	0.2	1	5	25

6.4.3 Preparation of Samples

All sample solutions were filtered using 20 ml plastic syringes and 0.45 µm nylon filters manufactured by National Scientific, before analysis on the ICP-OES. The process solutions and nickel and chromium drag-out rinse solutions were diluted with ultra pure water to make sure that the concentrations of the metals were within the calibration range. These dilution factors are shown in Table 6.10. The rinse solutions were stored in a refrigerator, and the process solutions were kept in a cooler box.

Table 6.10 Dilution factors of process and rinse solutions

Tank No.	Dilution factor
1,3,7,10,11,15,17	1000
16	200
20	20
21	20

6.5 Gravimetric Analysis of SS and TDS

Gravimetric analysis was carried out on all process and rinse solutions on the CPL. Samples for this analysis began on the 20/03.

Glass microfiber filters (Ahlstrom, 4.70 cm dia) were dried in an oven set at 105 ºC and 250 mL beakers were dried at 110 ºC. The filter papers and beakers were dried, cooled and weighed to a constant mass (i.e. the filter papers and beakers were weighed until consecutive readings differed by no more then 0.005 g)

Approximately 250 mL of the sample solution was shaken thoroughly and measured out in a measuring cylinder. The sample solution was filtered under suction (400 mmHg) into a glass Buchner flask. Suction was continued for 3 minutes after the bulk of the liquid had passed through the filter.

The filtered solution was poured from the flask to the pre-weighed 250 ml beaker and oven dried at approximately 110 ºC. When the liquid had evaporated and the solid residue was left on the bottom of the beaker, the beaker was removed from the oven cooled in a dessicator and weighed. After weighing, the beaker and residue were returned to the oven for 2 hours and reweighed. This process was continued until a constant mass was reached. The beakers were weighed to four decimal places on a Ohaus Adventurer Pro mass balance. The TDS content was calculated using Equation 6.1.

The sides of the filter paper holder were washed down with distilled water to capture all the solid particles. The filter was left to dry on the vacuum for about 2 minutes. The glass frit carrying the filter was removed from the apparatus and carried to the oven, the filter paper was removed gently with tweezers and placed in the oven set at 105 ºC. It was dried for 2 hours before cooling and reweighing. Then it was returned to the oven for 1 hour cooled and reweighed. This process continued until a constant mass was reached. The filter papers were weighed to four decimal places using an AJ Mettler mass balance. The SS content was calculated using Equation 6.2.

$$\text{TDS}\,(\text{g/L}) = \frac{[(\text{M}_2 - \text{M}_1) - \text{Blank 1}]\ (\text{g})}{\text{Volume}\,(\text{L})} \qquad \textit{Equation 6.1}$$

$$\text{SS}\ (\text{mg/L}) = \frac{[(\text{M}_2 - \text{M}_1) - \text{Blank 2}]\ (\text{g})}{\text{Volume}\,(\text{L})} \times \frac{1000\,\text{mg}}{1\,\text{g}} \qquad \textit{Equation 6.2}$$

M_1 is the mass of empty beaker/filter paper after drying (g)

M_2 is the mass of beaker/filter paper and solid residue after drying (g)

Blank 1 is the average mass of three 250 mL of ultra pure water samples which were treated in the same method as the samples.

Blank 2 is the average mass of three 250 mL of distilled water samples which were treated in the same method as the samples.

Method accuracy was checked using two standards, 100 mg/L standard solutions of NaCl (for TDS) and microcrystalline cellulose (for SS). The NaCl standard was prepared from a standard stock solution of 5000 mg/L which was made with ultra pure water. The 100 mg/L working analytical standard was freshly prepared every time the analysis was run. The 100 mg/L microcrystalline cellulose standard solution was prepared with distilled water. Approximately 0.1 g of the microcrystalline cellulose was accurately weighed out and left to dry overnight at 105 ºC. The standards were treated in the same way as the samples and run at the end of each analysis to check the accuracy of the method. The results for the NaCl and microcrystalline cellulose standards were within 4 % and 6 % of the expected values respectively.

6.6 Direct Reading Instrumental Analysis for Conductivity, TDS and pH

Measurements for conductivity, pH and TDS were conducted on the rinse solutions of the CPL. This was achieved using direct reading instruments, Hanna HI9033 Water multi-range conductivity meter; Hanna HI9025 microcomputer pH meter and Hanna, Dist WP 2, total dissolved solids meter. All instruments were calibrated before use, with appropriate standards shown in Table 6.11. These measurements were taken in the laboratory for ease of handling in a clean environment.

Table 6.11 Standard solutions used to calibrate the conductivity, pH and TDS instruments

Instrument	Calibration solution
Hanna HI9033, water multi-range conductivity meter	Hanna Instruments HIL 7031/500 1413µS/cm conductivity calibration
Hanna HI9025, microcomputer pH meter	BDH Laboratory Reagent, Buffer Solution, BD 190777D with pH 10 ±0.05 BD 190555B with pH 7 ±0.02 and BD190444A with pH 4 ±0.02
Hanna Dist WP 2, total dissolved solids meter	Hanna Instruments HIL 7032/500 EC/TDS 1382 mg/L (ppm) calibration solution

The density of a chromium bath solution is measured either in degree Baumé or specific gravity with a hydrometer. These measurements give a rough estimate of the chromic acid concentration of the bath.[4] A hydrometer (D0520/20C, 230 mm hydro, 0-50 Baumé) was used to measure the degree Baumé of the chromium solution (Tank 15). The hydrometer was placed into the tank and after letting it settle for about 5 minutes a reading was taken.

CHAPTER 7

RESULTS

In this chapter the results from the industrial monitoring of the CPL are presented in four sections. Existing (historical) data obtained from the company is discussed in Section 7.1. This data includes the results obtained from company documentation (Analysis Reports), directly from the line operators and from invoices issued by the Umgeni Municipality. Sections 7.2 to 7.3 present the new data obtained through measurement and observation. Section 7.2 presents the gravimetric (Tables 7.5 to 7.6) and elemental analysis (Tables 7.7 to 7.13) results for the CPL process solutions. Data for the rinse solutions are given in Section 7.3. This includes water flow rate results (Table 7.14) which were collected in order to estimate water usage on the CPL. Elemental analysis results are presented in Tables 7.15 to 7.28. These results together with those from Section 7.2 will be used to calculate the true cost of waste. The direct reading instrumental results for conductivity, pH and TDS and the gravimetric analysis results for TDS and SS are presented in Tables 7.29 to 7.42 for the rinse solutions. Finally in Section 7.4 the results for the product output, expressed as total surface area of the workpieces, processed in the CPL during the seventeen sample periods are given. These will be used in monitoring and targeting analysis and compared with the water economy diagrams in Figure 3.8.

7.1 Existing data on chemical additions and water consumption

Table 7.1 shows the date and quantity of chemical additions made to the seven process tanks. The additions were quoted in either units of mass or volume. The data recorded on the 16/02, 11/04 and 14/06 were obtained directly from the Analysis Reports. The information recorded on the 15/05 and 23/05 were documented by the line operators. The line operators were not certain of the exact amount of chemical added and this is indicated by NR (not recorded).

Table 7.1 Chemical additions to the process tanks in the CPL

Date	Tank No.	Tank	Chemical Additions	
			Chemical	Quantity added
16/02	1	Soak cleaner	HP 100	2.6 kg
	3	Electrocleaner	HP 16	1.8 kg
	10	Satin nickel	Nickel sulfate	17 kg
			Nickel chloride	1 kg
	15	Chromium plating	Chromic acid	17 kg
11/04	10	Satin nickel	Magnum 821	800 mL
	11	Bright nickel	Magnum 821	250 mL
15/05	1	Soak cleaner	HP 100	NR
	3	Electrocleaner	HP 16	NR
23/05	15	Chromium plating	Chromic acid	NR
14/06	3	Electrocleaner	HP 16	0.8 kg
	7	Galtin 140	Dry acid salts	1.2 kg
	10	Satin nickel	Nickel sulfate	9 kg
			Nickel chloride	3.3 kg
			Magnum 821	800 mL
			Boric acid	3.3 kg
			Leveller	8.8 L
	15	Chromium plating	Lumina 34	4.2 kg

Tables 7.2 to 7.4 show information taken from the Umgeni Municipality Tax Invoices for the three water meters installed on the factory premises. The first four entries show a pair of dates and their corresponding water meter reading. The fifth and sixth columns show the time period over which the water was consumed between those two dates. The final column shows the cost of the water consumed over that time period. This is based on the prevailing tariff (R7.15 per kL up to 15 May 2007, R7.58 per kL thereafter). Table 7.4 shows the water consumption for smelting and extrusion. The meter (102678) reads to a maximum of 10000 kL, then zeros and continues to measure water flow rate. The difference between reading of 9911 kL taken at 31/10/06 and the reading of 162 kL taken at 14/11/06 actually represents a volume of 251 kL of water used on the smelter and extrusion process.

Table 7.2 Water consumption from the Umgeni Municipality Tax Invoice for water meter 71237, Brass division

Date	Water meter reading (kL)	Date	Water meter reading (kL)	Time period (days)	Water Volume (kL)	Water Volume used per day (kL/day)	Cost (R)
30/06/06	19273	31/08/06	19884	62	611	9.85	4980.26
31/08/06	19884	31/10/06	20458	61	574	9.41	4678.67
31/10/06	20458	15/01/07	20558	76	100	1.32	815.10
15/01/07	20558	28/02/07	20971	44	413	9.39	3366.36
28/02/07	20971	31/03/07	21262	31	291	9.39	2371.94
31/03/07	21262	30/04/07	21835	30	573	19.1	4670.52
30/04/07	21835	15/05/07	22375	15	540	36.0	4401.54
15/05/07	22375	14/06/07	22829	30	454	15.1	3923.10
14/06/07	22829	16/07/07	23283	32	454	14.2	3923.10
16/07/07	23283	31/08/07	23383	46	100	2.17	864.12
31/08/07	23383	30/09/07	23722	30	339	11.3	2929.37

Table 7.3 Water consumption from the Umgeni Municipality Tax Invoice for water meter 834, Aluminium division

Date	Water meter reading (kL)	Date	Water meter reading (kL)	Time period (days)	Water Volume (kL)	Water Volume used per day (kL/day)	Cost (R)
18/10/06	2430	14/11/06	2664	27	234	8.67	1907.33
14/11/06	2664	15/12/06	2928	31	264	8.52	2151.86
15/12/06	2928	15/01/07	3011	31	83	2.68	676.53
15/01/07	3011	19/02/07	3314	35	303	8.66	2469.75
19/02/07	3314	15/03/07	3374	24	60	2.50	489.06
15/03/07	3374	16/04/07	3900	32	526	16.4	4287.43
16/04/07	3900	15/05/07	4195	29	295	10.2	2404.55
15/05/07	4195	14/06/07	4468	30	273	9.10	2359.05
14/06/07	4468	16/07/07	4672	32	204	6.38	1762.80
16/07/07	4672	20/08/07	4913	35	241	6.89	2082.53
20/08/07	4913	17/09/07	5167	28	254	9.07	2194.86

Table 7.4 Water consumption from the Umgeni Municipality Tax Invoice for water meter 102678, Smelting and Extrusion

Date	Water meter reading (kL)	Date	Water meter reading (kL)	Time period (days)	Water Volume (kL)	Water Volume used per day (kL/day)	Cost (R)
31/10/06	9911	14/11/06	162	14	251	17.9	2045.90
14/11/06	162	15/12/06	293	31	131	4.23	1067.78
15/12/06	293	28/02/07	612	75	319	4.25	2600.17
28/02/07	612	31/03/07	837	31	225	7.26	1833.98
31/03/07	837	30/04/07	1280	30	443	14.8	3610.89
30/04/07	1280	15/05/07	1780	15	500	33.3	4075.50
15/05/07	1780	14/06/07	1985	31	205	6.61	1771.45
14/06/07	1985	31/08/07	2200	79	215	2.72	1857.86
31/08/07	2200	30/09/07	2495	30	295	9.83	2549.15

Current data on water consumption could not be collected. Readings from the water meters installed by the Umgeni Municipality were difficult to obtain during on-site visits as the readings were obscured by condensation on the transparent covering of the meter. One of the water meters was deep in the ground and covered with soil and the transparent covering was slightly cracked, it was impossible to read the meter at all.

7.2 New data on Process Solutions

Table 7.5 displays the gravimetric analysis results for the pre-plating process solutions namely the soak cleaner (Tank 1), the electrocleaner (Tank 3) and the Galtin (Tank 7). In Table 7.6 are the gravimetric results for the satin and bright nickel solutions (Tanks 10 and 11 respectively), for the chromium plating solution (Tank 15) and the neutralizer (Tank 17). The Baumé readings taken for the chromium plating solution are also shown in Table 7.6, these measurements were taken from the 20/02. The sample collection for gravimetric analysis commenced on the 20/03 therefore there were no results for the previous 5 weeks as indicated by NM (not measured) in Table 7.6 .

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Table 7.5 Gravimetric TDS and SS measurements made on the pre-plating process solutions

Date	Tank 1		Tank 3		Tank 7	
	SS (mg/L)	TDS (g/L)	SS (mg/L)	TDS (g/L)	SS (mg/L)	TDS (g/L)
20/03	1.33	140	12.1	19.9	0	14.4
27/03	5.24	149	11	23.8	0	11.5
03/04	246	158	9.48	22.1	4.28	24.8
11/04	50.3	145	1.68	22.4	0	23.1
17/04	64.4	160	11.9	20.1	0	21.5
24/04	192	176	7.36	26.6	12.2	38.8
09/05	81.6	177	8.16	25.6	0	31.8
15/05	203	127	15.1	28.8	3.28	30.6
22/05	205	150	79.3	26.9	4.12	26.1
29/05	71.2	135	5.04	26.8	0	31.5
5/06	51.5	111	5.33	25.6	0	22.2
12/06	126	129	10.9	23.5	3.84	24.0
19/06	61.9	156	14.5	22.0	0	29.5

Table 7.6 Gravimetric TDS and SS measurements made on the plating and post plating process solutions

Date	Tank 10		Tank 11		Tank 15			Tank 17	
	SS (mg/L)	TDS (g/L)	SS (mg/L)	TDS (g/L)	SS (mg/L)	TDS (g/L)	Baumé	SS (mg/L)	TDS (g/L)
20/02	NM	NM	NM	NM	NM	NM	25	NM	NM
27/02	NM	NM	NM	NM	NM	NM	19	NM	NM
6/03	NM	NM	NM	NM	NM	NM	24	NM	NM
13/03	NM	NM	NM	NM	NM	NM	23	NM	NM
20/03	60.8	336	112	345	55.6	303	23	23.6	51.8
27/03	91.2	355	186	337	94.7	303	23	9.44	21.9
03/04	91.8	290	119	339	65.1	309	23	12.6	22.2
11/04	69.1	314	66	339	50.8	310	22	12.1	23.7
17/04	44.5	327	93.3	382	66.2	272	23	11.8	26.7
24/04	64.1	292	145	366	73.7	298	22	11.3	26.8
09/05	58.3	324	133	387	51.8	268	22	16	28.7
15/05	75.4	319	151	340	96.9	299	22	12.2	30.6
22/05	69.3	288	172	349	59.6	329	22	14.9	29.3
29/05	74.2	317	202	351	51.8	279	22	9.47	13.4
5/06	68.8	291	77.6	337	43.6	285	21	3.44	14.6
12/06	88.1	325	95.3	324	86.9	281	21	7.2	15.0
19/06	61.2	273	124	384	107	292	22	2.74	16.4

The average elemental concentrations (Ni, Cr, Na. S, B, P, Si, Fe, Cu, Zn, Pb) determined by ICP-OES for the process solution samples over the full monitoring period are displayed in Tables 7.7 to 7.13. The results are presented in order of increasing tank number. The results that were below the detection limit are indicated by BD in Tables 7.7 to 7.13.

Table 7.7 Average elemental concentrations (mg/L) in samples for Tank 1

Date	Na	P	Si	S	B	Pb	Zn	Cr	Fe	Cu	Ni
13/02	3481	3532	625	394	15.7	BD	26.0	12.0	12.9	BD	BD
20/02	6235	9334	1093	1368	15.1	37.2	80.7	13.1	22.5	7.00	BD
27/02	5553	5287	963	395	12.6	83.1	140	10.5	17.0	12.0	BD
06/03	5163	6297	866	422	11.4	BD	92.6	10.5	27.0	8.00	BD
13/03	5147	4815	880	468	46.1	40.7	65.7	17.3	19.5	9.00	BD
20/03	5110	4818	866	440	12.4	102	129	21.7	19.1	10.0	BD
27/03	6102	5796	1088	588	18.2	112	192	27.7	47.3	18.0	6.00
03/04	5980	5667	1110	554	112	63.9	71.3	29.9	23.0	BD	BD
11/04	5054	4622	1059	454	31.7	42.6	47.6	30.2	16.6	BD	BD
17/04	4580	4281	783	295	27.9	76.4	84.0	26.6	21.4	14.0	BD
24/04	5582	5344	1018	471	36.9	79.5	148	28.1	20.5	10.0	10.0
09/05	4761	4679	821	433	33.4	77.2	81.7	27.9	25.0	BD	BD
15/05	5801	5650	1019	471	17.6	161	151	33.0	26.5	14.0	BD
22/05	5391	5312	948	446	113	107	68.1	40.4	23.8	8.00	BD
29/05	4786	4565	847	409	29.0	117	130	36.6	22.6	8.00	6.00
5/06	4853	4706	842	420	51.4	104	81.0	40.0	23.0	BD	BD
12/06	5406	5376	918	449	23.1	106	49.0	36.3	23.9	BD	BD
19/06	5125	5000	896	436	36.1	94.8	108	37.1	23.9	BD	5.00

Table 7.8 Average elemental concentrations (mg/L) in samples for Tank 3

Date	Na	P	Si	S	B	Fe	Cr	Zn	Ni	Cu	Pb
13/02	818	589	180	125	13.3	8.31	0.53	BD	BD	BD	BD
20/02	1146	869	273	218	12.5	8.59	2.81	BD	BD	BD	BD
27/02	1061	665	211	136	18.9	9.38	38.6	BD	BD	BD	BD
06/03	1081	436	202	235	15.2	10.4	2.01	BD	BD	BD	BD
13/03	856	502	437	191	23.8	8.54	8.42	BD	BD	BD	BD
20/03	878	481	169	131	13.4	8.48	8.94	BD	BD	BD	BD
27/03	1123	683	217	149	44.0	8.86	2.62	BD	BD	BD	BD
03/04	967	652	271	144	100	10.0	8.54	BD	BD	BD	BD
11/04	1001	643	246	138	16.2	8.08	2.19	BD	BD	BD	BD
17/04	757	495	144	95.4	28.6	8.50	3.08	BD	BD	BD	BD
24/04	1124	866	518	174	32.8	9.03	5.54	BD	BD	BD	BD
09/05	1099	817	233	147	97.4	8.29	4.53	BD	BD	BD	BD
15/05	1268	975	291	158	28.4	10.4	3.81	BD	BD	BD	BD
22/05	1145	907	256	155	45.8	10.8	2.38	BD	BD	BD	BD
29/05	1068	815	233	139	30.6	8.64	1.65	BD	BD	BD	BD
5/06	1090	832	245	146	10.1	9.88	2.19	BD	BD	BD	BD
12/06	1028	821	222	126	14.2	11.1	2.71	BD	BD	BD	BD
19/06	962	696	234	175	12.0	8.31	2.89	BD	BD	BD	BD

Table 7.9 Average elemental concentrations (mg/L) in samples for Tank 7

Date	S	Na	B	Zn	Fe	Si	Pb	P	Cr	Ni	Cu
13/02	4460	602	16.0	24.4	30.9	15.0	13.5	65.8	4.00	4.00	BD
20/02	3727	371	36.4	18.4	26.8	8.15	9.51	1.18	4.00	4.00	BD
27/02	3933	389	17.1	26.0	24.8	9.24	17.3	6.12	5.00	5.00	BD
06/03	3555	359	231	31.6	33.5	23.9	16.3	10.9	9.00	9.00	BD
13/03	3613	360	59.2	44.3	29.8	9.11	12.2	58.6	15.0	15.0	BD
20/03	2926	292	48.1	57.6	36.8	13.8	20.0	13.2	14.0	14.0	7.00
27/03	6384	613	80.0	56.4	41.9	13.6	14.5	41.1	16.0	16.0	14.2
03/04	6272	601	31.3	55.1	42.5	23.3	14.7	19.9	14.0	14.0	8.00
11/04	6060	578	28.2	56.3	22.1	60.9	11.4	7.58	13.0	13.0	8.00
17/04	5214	509	120	81.5	31.6	20.3	19.3	18.5	12.0	12.0	22.0
24/04	9707	921	50.3	61.5	52.6	27.1	17.7	21.5	55.0	55.0	23.0
09/05	8600	795	24.7	84.8	77.0	21.9	82.0	32.7	40.0	40.0	22.0
15/05	7965	758	34.2	53.6	43.9	13.1	23.0	18.4	7.00	7.00	BD
22/05	7551	727	22.4	59.9	78.9	15.5	9.96	43.0	19.0	19.0	BD
29/05	6862	655	105	62.6	39.7	13.6	18.0	31.4	25.0	25.0	8.00
5/06	5844	560	32.4	54.8	48.1	18.0	11.6	22.5	26.0	26.0	7.00
12/06	5463	508	14.7	52.8	36.0	9.55	13.7	28.4	15.0	15.0	BD
19/06	7422	694	27.1	63.9	51.6	18.0	13.0	17.1	23.0	23.0	7.00

Table 7.10 Average elemental concentrations in samples for Tank 10

Date	g/L			mg/L							
	Ni	S	B	Na	Zn	Fe	P	Si	Cr	Cu	Pb
13/02	74.8	39.1	5.92	370	3.58	8.15	4.11	5.37	1.91	BD	BD
20/02	80.7	41.9	5.92	365	6.59	8.14	BD	8.38	1.44	BD	BD
27/02	81.5	42.7	5.77	354	4.05	8.19	BD	4.43	2.16	BD	BD
06/03	83.8	43.9	6.33	390	7.29	8.73	19.0	4.53	2.26	BD	BD
13/03	83.4	43.7	6.06	391	16.8	8.13	11.2	4.76	3.15	BD	BD
20/03	79.3	41.1	5.98	374	18.2	8.76	8.00	8.71	1.56	BD	BD
27/03	82.2	45.9	6.38	402	2.77	8.09	BD	7.20	2.89	BD	BD
03/04	64.9	36.4	4.88	328	81.7	8.08	2.21	15.5	2.59	BD	BD
11/04	82.0	46.1	6.31	403	4.43	8.10	BD	28.9	10.3	BD	BD
17/04	104	58.6	6.12	403	17.8	8.07	6.62	37.9	5.48	BD	BD
24/04	97.7	53.7	5.71	363	18.1	11.2	4.53	18.3	3.66	8	BD
09/05	105	45.0	6.00	388	23.9	10.4	6.49	35.1	2.49	14	BD
15/05	105	44.9	5.82	382	14.4	10.1	3.11	4.09	2.54	BD	BD
22/05	97.7	41.9	5.46	363	13.9	8.45	13.1	49.3	2.25	BD	BD
29/05	98.0	42.1	5.59	361	6.89	8.23	BD	2.64	1.56	BD	BD
5/06	104	44.2	5.67	368	8.14	8.72	6.86	8.96	1.74	BD	BD
12/06	93.7	39.9	5.36	346	7.78	8.06	BD	2.10	2.32	BD	BD
19/06	119	50.4	6.30	402	9.11	8.31	4.51	23.1	3.01	BD	BD

Table 7.11 Average elemental concentrations in samples for Tank 11

Date	g/L			mg/L							
	Ni	S	B	Na	Zn	Fe	Si	P	Cr	Cu	Pb
13/02	100	54.8	7.26	394	16.8	8.03	13.6	2.73	18.3	BD	BD
20/02	98.7	54.6	7.61	466	34.7	8.14	19.5	12.9	72.0	BD	BD
27/02	105	57.4	8.77	413	16.8	8.09	7.53	21.1	2.52	BD	BD
06/03	100	55.3	6.56	392	46.8	8.46	14.4	4.30	3.39	BD	BD
13/03	101	54.9	7.43	395	13.0	8.29	24.7	17.3	3.18	BD	BD
20/03	105	57.4	8.75	418	21.6	8.23	10.4	15.4	1.60	BD	BD
27/03	89.8	52.2	6.87	516	18.5	8.04	88.8	4.09	1.98	BD	BD
03/04	86.7	50.5	7.30	395	20.0	8.19	42.5	58.0	11.0	BD	BD
11/04	123	70.6	7.58	360	13.5	8.16	30.3	26.1	2.82	BD	BD
17/04	124	71.2	7.51	382	35.5	8.11	11.2	0.92	7.73	BD	BD
24/04	92.8	54.1	8.00	382	21.6	8.01	29.0	3.44	22.5	BD	BD
09/05	121	53.6	7.91	393	23.3	9.78	7.48	32.7	6.20	37.0	BD
15/05	123	54.7	6.25	414	13.1	8.34	7.86	8.67	7.49	BD	BD
22/05	117	51.5	5.86	385	14.4	8.24	6.78	0.34	4.52	BD	BD
29/05	102	45.6	5.14	326	11.7	8.47	9.16	5.41	2.02	BD	BD
5/06	114	50.7	5.64	364	11.2	8.37	7.31	5.49	2.84	BD	BD
12/06	120	52.4	5.77	369	14.7	8.03	4.57	13.5	2.86	BD	BD
19/06	124	54.1	5.73	385	20.7	8.38	62.9	14.5	1.76	14.0	BD

Table 7.12 Average elemental concentrations in samples for Tank 15

Date	g/L			mg/L							
	Cr	Ni	Cu	Na	B	S	Zn	P	Si	Fe	Pb
13/02	133	1.17	2.59	568	113	651	1030	1389	63.0	64.7	36.4
20/02	134	1.01	2.20	457	135	467	479	114	52.0	64.1	23.5
27/02	155	1.05	2.56	451	232	464	440	141	64.4	99.0	20.6
06/03	158	1.24	2.68	563	138	597	594	122	62.2	83.8	23.0
13/03	159	1.22	2.56	523	118	591	563	121	99.0	87.3	31.3
20/03	158	1.25	2.68	556	131	612	614	168	99.7	93.0	31.4
27/03	155	1.11	2.68	465	151	565	463	177	68.4	95.9	22.4
03/04	142	1.45	3.07	633	143	722	678	118	74.0	94.7	18.0
11/04	174	1.03	2.54	445	149	1814	443	116	62.2	70.3	15.2
17/04	163	1.05	2.44	417	133	480	422	121	57.7	65.8	18.0
24/04	172	1.50	2.50	500	143	755	602	123	59.8	81.4	16.1
09/05	139	1.19	2.46	493	121	1271	549	123	58.2	81.4	14.6
15/05	143	1.19	2.41	492	123	574	548	110	48.9	77.3	26.4
22/05	154	1.30	2.66	530	218	647	600	107	53.5	86.4	28.4
29/05	146	1.32	2.62	520	138	654	583	117	51.6	78.7	34.2
5/06	139	1.04	2.47	410	172	555	441	347	133	106	14.9
12/06	139	1.00	2.42	408	134	495	420	104	45.7	66.2	25.9
19/06	151	1.29	2.61	513	127	673	578	108	52.2	92.1	36.0

Table 7.13 Average elemental concentrations in samples for Tank 17

Date	g/L	mg/L									
	S	Cr	Na	B	Ni	Cu	Si	Fe	P	Zn	Pb
13/02	10.3	1820	860	94.0	52.1	62.5	15.2	11.1	108	23.4	BD
20/02	9.57	2550	794	77.0	66.9	67.3	3.30	13.1	14.9	21.5	BD
27/02	33.4	421	1681	129	12.5	6.30	11.0	17.8	40.4	0.08	BD
06/03	23.1	998	1723	108	33.2	11.1	4.90	43.0	0.06	8.29	BD
13/03	20.8	2190	1596	76.9	64.7	53.9	2.74	27.6	46.9	46.7	17.0
20/03	19.3	3410	1526	84.0	52.8	90.7	4.31	15.4	11.3	33.5	BD
27/03	9.38	369	694	215	58.6	1.87	1.63	39.0	8.71	13.0	15.9
03/04	9.21	991	712	331	47.6	77.7	40.0	12.2	1.05	13.4	22.0
11/04	8.78	1400	688	65.8	33.0	36.8	2.81	9.67	11.9	20.0	18.3
17/04	5.79	2400	554	99.0	106	115	2.74	9.47	23.8	44.7	BD
24/04	7.80	2580	637	155	54.3	64.4	6.21	11.7	19.2	22.5	19.1
09/05	7.46	3280	623	28.8	88.9	145	9.35	12.6	28.4	42.0	13.8
15/05	6.50	3470	578	168	77.7	95.6	5.64	11.8	19.2	37.3	BD
22/05	6.67	1760	601	57.8	64.3	76.6	6.40	9.92	6.39	37.3	BD
29/05	5.60	433	418	155	409	5.07	1.85	10.8	5.06	11.2	BD
5/06	5.20	866	400	71.7	74.4	10.7	1.80	11.0	8.52	8.39	BD
12/06	4.85	1570	387	17.7	30.2	36.5	0.86	10.8	5.59	21.2	BD
19/06	4.51	1720	368	58.3	55.1	37.1	4.67	10.3	17.6	19.2	BD

7.3 New data on Rinse Solutions

This section presents the monitoring results from the rinse solutions. Table 7.14 displays the volumetric flow rates of incoming water (through the taps) supplying fresh water to the flowing rinse tanks.

Tables 7.15 to 7.28 represent the average elemental concentrations for the rinse solutions. The soak cleaner rinse (Tank 2) and the electrocleaner countercurrent rinse (Tanks 4-6) results are shown in Tables 7.15 and 7.16 to 7.18 respectively. The Galtin countercurrent rinse (Tanks 8-9) results are given in Tables 7.19 to 7.20. The nickel countercurrent rinse (Tanks 12-14) and drag-out rinse (Tanks 20 and 21) results are shown in Tables 7.21 to 7.23 and 7.27 to 7.28 respectively. The chromium drag-out rinse (Tank 16) and neutralizer rinse (Tank 18) results are shown in Tables 7.24 and 7.25 respectively. Table 7.26 presents the hot water rinse (Tank 19) results. The results that were below the detection limit are indicated by BD in Tables 7.15 to 7.28.

Tables 7.29 to 7.42 display the conductivity, pH, TDS and SS readings taken for the rinse solutions. This includes conductivity, pH and TDS results from direct reading instruments and TDS and SS measurements from gravimetric analysis.

Table 7.14 Rinse water flow rates

Date	Tank No.	Tank receiving water	Flow rate (L/min)
13/02	2	Soak cleaner rinse	0.92
	6	Electrocleaner rinse	0.72
	9	Galtin rinse	0.39
	14	Nickel rinse	0.35
	18	Neutralizer rinse	0.39
20/02	2	Soak cleaner rinse	0.65
	6	Electrocleaner rinse	1.00
	9	Galtin rinse	1.16
	14	Nickel rinse	2.76
	18	Neutralizer rinse	1.60
27/02	2	Soak cleaner rinse	1.89
	6	Electrocleaner rinse	1.50
	9	Galtin rinse	0.34
	14	Nickel rinse	1.33
	18	Neutralizer rinse	3.00
6/03	2	Soak cleaner rinse	0.82
	6	Electrocleaner rinse	0.95
	9	Galtin rinse	0.82
	14	Nickel rinse	1.29
	18	Neutralizer rinse	1.33
13/03	2	Soak cleaner rinse	0.4
	6	Electrocleaner rinse	0.4
	9	Galtin rinse	0.75
	14	Nickel rinse	1.33
	18	Neutralizer rinse	4.0
20/03	2	Soak cleaner rinse	0.92
	6	Electrocleaner rinse	0.21
	9	Galtin rinse	0.11
	14	Nickel rinse	0.58
	18	Neutralizer rinse	1.38
27/03	2	Soak cleaner rinse	0.75
	6	Electrocleaner rinse	1.57
	9	Galtin rinse	0.24
	14	Nickel rinse	0.63
	18	Neutralizer rinse	0.12
3/04	2	Soak cleaner rinse	1.44
	6	Electrocleaner rinse	0.95
	9	Galtin rinse	0.13
	14	Nickel rinse	0.25
	18	Neutralizer rinse	0.19

Table 7.14 Rinse water flow rates Continued

Date	Tank No.	Tank receiving water	Flow rate (L/min)
11/04	2	Soak cleaner rinse	2.77
	6	Electrocleaner rinse	0.84
	9	Galtin rinse	Tap closed
	14	Nickel rinse	0.35
	18	Neutralizer rinse	0.25
17/04	2	Soak cleaner rinse	2.25
	6	Electrocleaner rinse	0.5
	9	Galtin rinse	0.35
	14	Nickel rinse	0.21
	18	Neutralizer rinse	0.38
25/04	2	Soak cleaner rinse	0.63
	6	Electrocleaner rinse	0.75
	9	Galtin rinse	Tap closed
	14	Nickel rinse	0.92
	18	Neutralizer rinse	Tap closed
9/05	2	Soak cleaner rinse	4.5
	6	Electrocleaner rinse	2.25
	9	Galtin rinse	0.20
	14	Nickel rinse	0.34
	18	Neutralizer rinse	0.86
15/05	2	Soak cleaner rinse	3.6
	6	Electrocleaner rinse	0.86
	9	Galtin rinse	0.18
	14	Nickel rinse	1.2
	18	Neutralizer rinse	0.29
22/05	2	Soak cleaner rinse	1.50
	6	Electrocleaner rinse	0.46
	9	Galtin rinse	0.10
	14	Nickel rinse	0.46
	18	Neutralizer rinse	0.38
29/05	2	Soak cleaner rinse	4.50
	6	Electrocleaner rinse	0.60
	9	Galtin rinse	0.71
	14	Nickel rinse	0.19
	18	Neutralizer rinse	0.75
5/06	2	Soak cleaner rinse	1.64
	6	Electrocleaner rinse	1.16
	9	Galtin rinse	0.18
	14	Nickel rinse	1.71
	18	Neutralizer rinse	0.12

Table 7.14 Rinse water flow rates Continued

Date	Tank No.	Tank receiving water	Flow rate (L/min)
12/06	2	Soak cleaner rinse	2.57
	6	Electrocleaner rinse	0.50
	9	Galtin rinse	0.38
	14	Nickel rinse	1.44
	18	Neutralizer rinse	0.32
19/06	2	Soak cleaner rinse	1.13
	6	Electrocleaner rinse	0.75
	9	Galtin rinse	0.40
	14	Nickel rinse	0.67
	18	Neutralizer rinse	0.24

Table 7.15 Average elemental concentrations in samples for Tank 2

Date	mg/L				µg/L						
	Na	P	Si	S	B	Cr	Cu	Fe	Ni	Zn	Pb
13/02	8.16	7.16	1.79	1.19	17.9	14.9	245	48.8	19.3	329	107
20/02	46.5	31.2	7.93	4.18	47.7	53.5	126	79.8	4.8	259	171
27/02	6.47	6.74	1.23	1.06	15.4	15.9	42.9	33.5	12.1	118	45.9
06/03	23.0	17.8	3.86	2.67	33.7	83.1	25.0	38.3	2.8	37.2	60.1
13/03	40.8	21.0	6.89	3.44	71.7	125	62.1	72.1	6.0	117	165
20/03	66.6	50.3	11.1	5.63	105	213	185	132.8	19.6	587	506
27/03	75.2	60.0	13.3	6.44	108	218	172	133.0	18.5	671	1155
03/04	31.9	15.2	5.71	3.10	61.7	124	37.3	57.1	8.6	58.7	257
11/04	44.7	1.35	0.81	1.15	12.7	5.7	10.1	22.2	4.0	5.5	BD
17/04	56.5	36.2	9.31	4.62	123	276	94.2	95.2	20.7	264	693
24/04	84	72.8	15.3	7.48	204	369	326	151	41.6	981	1433
09/05	13.4	4.56	2.35	1.51	37.7	74.7	36.6	59.9	7.6	167	117
15/05	48.1	28.7	8.12	3.96	181	236	41.7	146	20.0	72.5	255
22/05	30.9	13.9	5.52	2.72	140	213	19.5	121	15.6	18.7	144
29/05	31.1	14.0	5.49	2.60	207	213	24.9	90.4	14.9	30.3	145
5/06	38.8	22.5	6.62	3.53	142	298	41.1	106	18.4	64.4	259
12/06	26.3	11.6	4.53	2.40	89.9	146	12.6	62.8	10.0	5.2	96.8
19/06	49.2	31.8	8.23	4.21	140	281	40.8	103	28.6	85.6	297

Table 7.16 Average elemental concentrations in samples for Tank 4

Date	mg/L				µg/L						
	Na	P	Si	S	B	Cr	Cu	Fe	Ni	Zn	Pb
13/02	4.63	2.96	8.07	6.03	84.2	180	508	75.9	12.4	225	509
20/02	4.31	2.43	1.08	1.06	22.7	8.69	14.5	21.5	39.1	24.0	BD
27/02	1.93	0.80	0.54	1.08	37.6	3.81	5.94	16.6	68.0	1.33	BD
06/03	4.30	2.40	0.97	1.28	14.8	8.74	12.1	21.6	10.4	12.1	BD
13/03	7.81	4.36	1.62	1.70	29.1	26.1	27.0	20.7	37.8	38.6	BD
20/03	6.31	3.63	1.35	1.36	24.7	17.5	15.9	22.2	22.4	15.3	BD
27/03	8.22	4.73	1.76	1.44	35.2	15.8	10.9	14.0	28.4	13.6	BD
03/04	4.37	2.42	1.09	1.25	20.2	14.8	2.48	12.2	BD	BD	BD
11/04	3.41	1.93	1.13	1.35	22.7	11.6	73.8	12.6	BD	BD	BD
17/04	12.6	7.52	2.60	2.17	38.6	35.0	17.4	17.9	8.77	16.7	BD
24/04	9.76	6.28	2.31	2.19	39.1	31.8	14.7	16.5	11.0	21.2	BD
09/05	3.08	1.80	0.96	1.05	25.0	8.03	4.54	11.8	BD	BD	BD
15/05	4.10	2.51	1.29	1.02	38.8	9.26	1.11	12.5	11.3	BD	BD
22/05	5.85	3.82	1.68	0.95	28.9	15.2	4.47	15.2	9.57	BD	BD
29/05	2.68	1.68	0.98	0.79	22.5	8.52	BD	12.6	BD	BD	BD
5/06	2.25	1.15	0.89	0.79	28.0	8.33	BD	13.3	BD	BD	BD
12/06	2.20	1.21	0.90	2.68	26.4	9.37	2.65	15.1	7.95	BD	BD
19/06	5.15	3.26	1.53	1.22	33.6	81.6	23.9	16.8	41.1	BD	BD

Table 7.17 Average elemental concentrations (µg/L) in samples for Tank 5

Date	Na	S	Si	P	B	Fe	Ni	Cr	Cu	Zn	Pb
13/02	503	938	441	68.3	8.78	36.3	7.47	4.54	105	72.3	BD
20/02	587	668	348	91.3	6.90	18.6	13.2	3.47	31.9	18.0	BD
27/02	524	965	272	56.2	22.2	22.2	155	2.80	BD	BD	BD
06/03	758	995	301	292	10.6	15.6	7.13	3.66	11.5	BD	BD
13/03	773	1027	324	121	20.9	13.3	68.1	7.81	8.25	BD	BD
20/03	721	756	304	137	13.6	14.6	8.48	4.87	12.6	4.07	BD
27/03	931	919	393	158	16.1	11.4	29.6	4.56	BD	BD	BD
03/04	640	3058	366	93.2	11.8	11.9	9.55	10.6	10.7	BD	BD
11/04	580	1183	362	45.8	12.3	11.3	18.2	3.34	BD	BD	BD
17/04	1295	1292	496	486	17.3	19.4	6.44	10.6	BD	BD	BD
24/04	1113	1618	485	355	22.9	11.4	10.1	8.54	BD	BD	BD
09/05	516	713	415	205	15.4	11.7	12.1	11.3	BD	9.24	BD
15/05	597	673	489	286	19.4	11.1	39.1	5.07	BD	BD	BD
22/05	701	538	524	196	10.5	11.2	4.64	5.01	BD	BD	BD
29/05	517	741	484	51.2	10.8	11.1	4.66	2.55	BD	BD	BD
5/06	530	684	504	124	6.88	11.1	BD	3.35	BD	BD	BD
12/06	508	575	506	69.2	18.0	11.2	4.59	2.19	BD	BD	BD
19/06	658	728	538	114	9.81	11.2	BD	11.2	BD	BD	BD

Table 7.18 Average elemental concentrations (µg/L) in samples for Tank 6

Date	Na	S	Si	P	B	Fe	Ni	Cr	Cu	Zn	Pb
13/02	473	961	437	62.6	6.3	22.8	8.27	1.19	70.6	54.1	BD
20/02	477	4593	323	38.2	13.6	19.2	BD	1.56	24.1	BD	BD
27/02	505	967	268	45.3	22.3	19.6	195	1.95	BD	BD	BD
06/03	546	1277	254	22.3	15.0	15.8	7.19	5.61	BD	BD	BD
13/03	509	787	269	37.4	8.6	14.3	9.63	4.14	15.2	6.99	BD
20/03	517	683	272	43.3	8.4	13.1	BD	4.00	BD	BD	BD
27/03	631	1014	353	49.6	21.5	11.7	103	4.13	BD	BD	BD
03/04	543	1181	359	30.6	8.8	11.5	6.90	8.06	BD	BD	BD
11/04	560	1457	430	102.0	7.7	12.2	9.41	2.66	BD	BD	BD
17/04	739	1233	399	93.3	13.5	12.0	6.48	6.62	BD	BD	BD
24/04	574	1325	398	77.3	20.5	12.4	12.01	4.91	19.9	7.27	BD
09/05	476	725	451	67.7	8.1	11.8	BD	1.77	BD	BD	BD
15/05	460	522	461	35.6	10.5	11.0	9.94	1.98	BD	BD	BD
22/05	544	528	492	82.7	9.8	11.0	BD	7.47	BD	BD	BD
29/05	489	1011	474	34.8	6.1	11.0	1.04	2.20	BD	BD	BD
5/06	465	686	509	57.9	5.9	11.4	BD	4.10	BD	BD	BD
12/06	438	531	491	46.3	5.2	11.1	BD	1.59	BD	BD	BD
19/06	490	646	501	61.0	9.6	11.1	BD	56.3	BD	BD	BD

Table 7.19 Average elemental concentrations in samples for Tank 8

Date	mg/L		µg/L								
	S	Na	Si	Ni	Zn	P	Cu	Fe	B	Cr	Pb
13/02	39.2	3.56	513	5780	270	150	115	161	411	21.6	BD
20/02	26.7	2.70	368	207	187	263	39.3	72.0	18.6	17.1	BD
27/02	36.0	3.49	338	1161	308	69.8	93.7	144	90.0	24.5	39.7
06/03	25.6	2.63	304	219	253	41.1	24.3	87.3	24.5	52.3	BD
13/03	27.6	2.79	325	599	483	43.6	83.6	84.3	43.6	36.7	BD
20/03	40.1	3.92	357	375	632	83.8	148	245	28.2	50.9	47.8
27/03	109.6	9.56	558	622	791	317	161	656	43.4	72.3	171
03/04	68.2	6.07	481	467	591	134	290	366	41.9	63.4	58.3
11/04	64.6	5.82	537	482	683	110	197	364	32.6	66.1	53.0
17/04	74.7	7.01	752	265	1570	675	206	375	99.3	111	52.9
24/04	374	22.13	1153	1167	1753	880	483	2397	1083	268	137
09/05	101	8.77	562	415	683	332	188	613	48.5	88.7	64.5
15/05	118	10.39	710	708	995	481	204	541	106	131	BD
22/05	106	9.45	721	363	846	443	79.0	454	66.4	123	BD
29/05	35.2	3.38	563	523	315	65.0	72.2	166	31.3	40.4	BD
5/06	50.3	4.64	603	551	572	88.0	127	295	39.8	61.6	61.1
12/06	56.9	5.17	630	1016	589	243	69.0	427	66.0	64.9	53.4
19/06	112	9.99	740	56	1032	599	143	559	113	173	BD

Table 7.20 Average elemental concentrations (µg/L) in samples for Tank 9

Date	S	Na	Si	Ni	Zn	P	Cu	Fe	B	Cr	Pb
13/02	3302	573	448	2354	19.1	29.4	13.4	18.6	193	2.13	BD
20/02	1490	511	329	40.9	BD	14.7	10.7	16.3	11.7	6.04	BD
27/02	1120	477	263	114	5.93	17.1	BD	20.3	21.4	3.54	BD
06/03	3196	636	276	604	11.0	30.5	BD	20.9	56.0	3.46	BD
13/03	1431	498	267	105	BD	15.1	BD	15.7	18.9	6.09	BD
20/03	2647	610	262	166	17.9	22.7	8.9	19.9	28.6	6.02	BD
27/03	5338	815	353	181	8.15	450	BD	13.3	23.5	3.65	BD
03/04	3227	655	351	254	7.19	28.1	BD	11.5	30.2	59.8	BD
11/04	2780	625	360	119	6.45	35.3	BD	11.8	20.0	3.62	BD
17/04	4682	852	398	42.1	19.8	98.1	BD	13.9	12.8	6.65	BD
24/04	15279	1693	412	448	78.4	30.7	20.1	11.5	44.1	5.91	BD
09/05	5717	920	455	86.9	13.3	132	8.6	11.6	28.6	7.47	BD
15/05	6429	931	485	831	19.4	17.6	BD	11.2	75.3	5.03	BD
22/05	5796	927	507	174	17.9	20.7	BD	11.3	35.3	5.77	BD
29/05	5842	575	496	115	BD	34.0	BD	13.7	14.9	1.87	BD
5/06	2674	603	540	93.8	BD	30.1	BD	12.4	20.3	5.93	BD
12/06	2574	618	522	399	BD	32.5	BD	11.4	43.6	2.08	BD
19/06	5949	908	527	458	21.4	32.8	BD	11.3	43.2	8.81	BD

Table 7.21 Average elemental concentrations in samples for Tank 12

Date	(mg/L)		(µg/L)								
	Ni	S	B	Na	Si	Cr	P	Fe	Cu	Zn	Pb
13/02	8.22	4.56	666	464	432	31	27.4	10.8	BD	BD	BD
20/02	5.66	3.41	460	469	318	237	17.6	11.3	BD	BD	BD
27/02	5.82	4.07	526	516	261	300	20.9	13.0	BD	BD	BD
06/03	12.7	6.89	991	511	279	45	50.0	13.7	BD	BD	BD
13/03	7.85	4.32	604	468	252	57	12.5	10.1	BD	BD	BD
20/03	13.6	7.24	911	549	253	321	45.0	10.5	BD	BD	BD
27/03	12.4	6.37	886	508	322	269	66.0	9.7	BD	BD	BD
03/04	1.38	1.59	207	435	327	26	76.3	9.7	BD	BD	BD
11/04	1.85	1.79	287	460	344	8	31.7	9.8	BD	BD	BD
17/04	21.1	10.2	1517	557	371	225	33.7	9.7	BD	BD	BD
24/04	16.7	8.12	1162	521	364	22	88.3	9.5	BD	BD	BD
09/05	2.54	1.80	289	442	442	4	27.3	9.8	BD	BD	BD
15/05	24.4	11.3	1397	546	460	49	27.7	9.7	BD	BD	BD
22/05	27.1	12.6	1711	561	480	102	42.6	9.6	BD	BD	BD
29/05	16.7	8.18	1212	491	506	34	49.8	9.6	BD	BD	BD
5/06	4.79	3.02	537	448	471	16	23.0	9.6	41.5	BD	BD
12/06	4.06	2.65	384	440	488	19	125.9	9.9	BD	BD	BD
19/06	26.0	12.3	1760	531	502	19	43.8	9.6	BD	BD	BD

Table 7.22 Average elemental concentrations in samples for Tank 13

Date	mg/L		µg/L								
	Ni	S	B	Na	Si	Cr	P	Fe	Cu	Zn	Pb
13/02	4.49	2.78	406	448	430	23.7	13.7	12.3	24.1	BD	BD
20/02	6.15	3.66	514	468	311	137	27.4	10.9	BD	BD	BD
27/02	5.66	3.91	462	530	262	290	27.3	13.0	BD	BD	BD
06/03	6.01	3.64	493	466	260	25.8	6.7	11.6	BD	BD	BD
13/03	3.72	2.52	325	454	258	80.7	19.8	10.9	BD	BD	BD
20/03	11.4	6.11	779	511	247	375	36.1	10.9	BD	BD	BD
27/03	7.38	4.50	654	478	325	301	607	12.0	BD	BD	BD
03/04	1.19	4.52	186	736	339	12.6	23.3	10.6	BD	BD	BD
11/04	3.22	2.43	360	479	372	8.7	14.2	9.67	BD	BD	BD
17/04	18.8	9.14	1423	545	378	125	75.4	11.1	BD	BD	BD
24/04	1.40	1.27	196	414	437	3.6	127	10.2	BD	BD	BD
09/05	12.0	6.23	908	503	369	16.2	35.4	9.78	7.17	BD	BD
15/05	18.0	8.89	1098	525	459	53.8	49.5	9.51	BD	BD	BD
22/05	12.8	6.81	1003	515	485	70.8	49.0	9.55	BD	BD	BD
29/05	10.2	5.44	833	470	477	11.0	75.4	9.55	BD	BD	BD
5/06	6.52	3.61	569	445	488	12.6	27.9	9.48	BD	BD	BD
12/06	12.2	6.19	913	471	499	28.3	60.6	9.47	BD	BD	BD
19/06	22.9	10.8	1543	514	503	31.8	38.5	9.62	BD	BD	BD

Table 7.23 Average elemental concentrations (µg/L) in samples for Tank 14

Date	Ni	S	B	Na	Si	Cr	P	Fe	Cu	Pb	Zn
13/02	404	713	53	421	424	8	22	15	52	BD	BD
20/02	6077	3681	475	465	341	66	14	11	BD	BD	BD
27/02	1514	2201	153	505	264	218	29	14	BD	BD	BD
06/03	304	867	58	535	268	21	30	12	BD	BD	BD
13/03	651	896	73	422	250	14	22	30	BD	BD	BD
20/03	2635	2093	233	465	244	367	15	11	BD	BD	BD
27/03	1119	1396	143	466	448	211	31	10	BD	BD	BD
03/04	8	569	88	428	333	7	20	10	BD	BD	BD
11/04	122	715	60	420	343	5	32	10	BD	BD	BD
17/04	11707	6264	913	490	368	86	21	10	BD	BD	BD
24/04	2603	2029	238	446	371	7	21	11	BD	BD	BD
09/05	139	547	54	418	431	2	28	10	BD	BD	BD
15/05	14404	7362	919	516	466	118	82	61	BD	BD	BD
22/05	5424	3484	495	471	484	30	17	10	BD	BD	BD
29/05	532	734	84	414	484	3	17	10	BD	BD	BD
5/06	764	970	96	419	473	6	28	10	BD	BD	BD
12/06	5537	3175	441	437	513	12	38	10	BD	BD	BD
19/06	12442	6610	943	480	502	24	48	10	BD	BD	BD

Table 7.24 Average elemental concentrations in samples for Tank 16

Date	g/L	mg/L									
	Cr	Cu	Ni	Na	S	Fe	Zn	Pb	P	B	Si
13/02	13.8	304	136	135	94.5	91.5	77.4	85.9	125	18.0	11.9
20/02	19.5	405	185	155	108	94.0	98.7	88.4	92.8	41.3	12.8
27/02	19.2	395	181	153	120	94.8	97.4	86.0	75.7	22.9	11.4
06/03	16.9	339	166	143	118	96.4	86.6	86.5	63.6	30.2	18.7
13/03	18.3	337	156	143	114	93.8	83.3	87.1	50.2	27.4	8.12
20/03	20.2	362	170	147	125	97.0	90.2	88.5	52.9	24.1	9.11
27/03	18.8	349	166	146	124	98.2	84.3	87.0	39.1	27.2	10.9
03/04	17.9	337	158	146	126	94.6	86.8	86.6	45.8	24.8	12.1
11/04	15.9	297	144	136	104	94.1	74.2	87.4	32.0	20.5	7.45
17/04	20.0	324	167	139	109	94.7	80.2	85.8	30.3	18.2	8.21
24/04	22.2	355	169	144	119	95.9	89.5	87.2	39.0	18.9	9.07
09/05	17.3	276	136	130	104	92.3	69.5	85.8	19.9	35.0	6.93
15/05	19.0	250	122	128	80.0	91.8	62.5	86.4	42.9	22.6	9.77
22/05	21.6	315	155	137	90.8	94.6	79.7	86.7	23.3	32.5	7.59
29/05	16.7	249	126	125	76.8	90.4	62.8	88.0	22.9	75.9	6.28
5/06	14.5	219	111	119	64.9	89.1	55.3	86.4	14.0	48.7	5.21
12/06	13.7	208	105	119	61.7	89.2	51.4	85.0	13.3	38.2	5.75
19/06	15.6	237	119	123	69.5	91.4	69.7	86.3	15.1	24.1	6.24

Table 7.25 Average elemental concentrations in samples for Tank 18

Date	mg/L	µg/L									
	S	Na	Si	Cr	Ni	B	P	Fe	Zn	Pb	Cu
13/02	9.77	1216	419	48	27	24	12	10	BD	BD	BD
20/02	16.8	1821	305	925	79	47	10	15	BD	BD	BD
27/02	11.6	1240	253	92	152	43	11	14	BD	BD	BD
06/03	78.0	6652	253	**4134**	244	34	87	42	58	BD	BD
13/03	12.8	1392	255	223	82	31	7	11	BD	BD	BD
20/03	22.6	2174	235	148	124	34	74	10	BD	BD	BD
27/03	16.9	1670	321	313	40	54	22	10	BD	BD	BD
03/04	6.21	872	323	305	80	42	18	11	BD	BD	BD
11/04	7.50	1017	349	24	156	53	9	10	8	BD	BD
17/04	11.7	1420	359	233	50	31	23	10	BD	BD	BD
24/04	25.1	2586	355	208	117	108	17	10	BD	BD	BD
09/05	5.36	903	460	184	63	33	33	9	BD	BD	BD
15/05	3.14	696	435	80	160	64	46	10	BD	BD	BD
22/05	10.6	1386	469	180	143	37	21	9	BD	BD	BD
29/05	2.88	601	473	20	64	32	11	10	BD	BD	BD
5/06	12.8	1385	475	191	74	97	15	10	BD	BD	BD
12/06	5.87	868	491	89	181	43	12	10	BD	BD	BD
19/06	20.8	2148	490	414	200	118	23	10	BD	BD	BD

Table 7.26 Average elemental concentrations in samples for Tank 19

Date	mg/L	µg/L									
	S	Na	Si	Cr	Ni	B	P	Fe	Zn	Pb	Cu
13/02	3.85	707	574	225	605	156	11	10	12	BD	BD
20/02	6.43	972	637	588	669	261	23	10	BD	BD	BD
27/02	10.9	1138	341	1591	479	123	13	10	BD	BD	BD
06/03	20.8	1881	424	2777	1024	215	48	10	46	BD	BD
13/03	5.98	843	308	400	290	138	24	10	BD	BD	BD
20/03	12.1	1343	338	1437	839	250	7	10	9	BD	BD
27/03	7.41	1386	406	464	446	420	410	464	5	BD	BD
03/04	13.7	1868	462	420	1879	421	483	420	5	BD	BD
11/04	17.2	1879	550	2859	1647	564	29	11	12	BD	BD
17/04	17.1	1924	565	2341	1354	706	35	10	18	BD	BD
24/04	4.81	983	490	1549	144	269	59	10	BD	BD	BD
09/05	7.24	1603	615	420	2003	421	374	420	BD	BD	BD
15/05	9.33	1574	712	3435	254	528	139	10	BD	BD	BD
22/05	1.90	766	613	1104	24	183	43	10	BD	BD	BD
29/05	6.51	1376	848	2451	134	399	44	10	BD	BD	BD
5/06	12.8	1848	1028	3696	557	721	25	10	BD	BD	BD
12/06	3.97	925	730	1346	388	336	1951	10	20	BD	BD
19/06	1.12	944	514	420	68	424	157	420	BD	BD	BD

Table 7.27 Average elemental concentrations (mg/L) in samples for Tank 20

Date	Ni	S	B	Na	Fe	Pb	Si	P	Zn	Cr	Cu
13/02	1190	622	99.6	13.9	8.39	8.49	0.451	1.21	0.082	0.0572	BD
20/02	1006	530	88.3	13.4	8.39	8.45	0.789	0.312	BD	0.0936	BD
27/02	1752	914	140	16.1	8.39	8.41	0.428	0.583	0.102	0.0717	BD
06/03	1378	746	110	14.6	8.39	8.49	0.394	0.498	0.128	0.0609	BD
13/03	1716	814	122	15.1	8.39	8.43	0.427	0.399	0.040	0.0795	BD
20/03	1864	898	129	15.6	8.39	8.45	0.532	0.425	0.001	0.123	BD
27/03	1640	854	136	16.0	8.39	8.43	0.382	0.625	0.036	0.155	BD
03/04	1732	906	133	15.9	8.39	8.48	0.466	0.527	0.097	0.108	BD
11/04	1240	706	101	14.0	8.39	8.44	1.18	0.257	0.428	0.161	BD
17/04	2200	1274	147	14.5	8.38	8.46	0.455	0.285	0.267	0.0985	BD
24/04	1774	1000	105	14.6	8.39	8.50	0.403	0.535	0.419	0.0815	BD
09/05	1006	436	52.3	11.3	8.41	8.64	0.590	0.483	0.577	0.0673	BD
15/05	788	340	60.2	11.9	8.38	8.47	0.353	0.316	0.416	0.191	BD
22/05	1486	642	90.7	13.6	8.39	8.42	0.365	0.198	0.106	0.0747	BD
29/05	1586	686	96.8	13.9	8.39	8.43	0.418	0.310	0.174	0.227	BD
5/06	916	396	60.1	11.6	8.39	8.40	0.434	0.345	0.068	0.0882	BD
12/06	868	378	57.2	11.5	8.39	8.41	0.452	0.378	0.058	0.0363	BD
19/06	912	398	58.4	11.7	8.39	8.48	0.432	0.294	BD	0.380	BD

Table 7.28 Average elemental concentrations (mg/L) in samples for Tank 21

Date	Ni	S	B	Na	Fe	Pb	Si	P	Zn	Cr	Cu
13/02	1046	568	93.2	12.1	8.39	8.44	0.704	0.411	0.178	0.130	BD
20/02	832	450	76.2	11.5	8.39	8.43	0.594	0.478	0.092	0.029	BD
27/02	860	464	77.9	11.5	8.39	8.44	0.498	0.213	0.056	0.034	BD
06/03	814	428	68.2	11.3	8.39	8.50	0.571	0.263	0.088	0.033	BD
13/03	1248	594	93.5	12.4	8.39	8.42	0.688	0.467	0.083	0.052	BD
20/03	1210	572	91.8	12.2	8.39	8.42	0.575	0.380	0.040	0.115	BD
27/03	1168	614	101	12.5	8.39	8.45	0.537	0.400	0.115	0.103	BD
03/04	1106	564	89.3	12.2	8.39	8.43	0.711	0.366	0.023	0.086	BD
11/04	876	514	82.0	11.8	8.38	8.42	0.576	0.086	0.218	0.102	BD
17/04	1658	942	98.7	13.9	8.42	8.73	0.360	0.695	0.289	0.092	BD
24/04	3740	2100	234	18.1	8.39	8.48	0.597	0.688	0.504	0.127	BD
09/05	2320	1020	159	14.9	8.39	8.44	0.647	0.658	0.303	0.088	BD
15/05	2200	976	149	14.5	8.39	8.41	0.473	0.649	0.234	0.071	BD
22/05	2660	1150	177	15.6	8.39	8.45	0.507	0.544	0.299	0.085	BD
29/05	2840	1226	184	16.1	8.39	8.45	1.841	0.328	0.419	0.092	BD
5/06	2260	990	151	14.8	8.39	8.45	0.544	0.744	0.265	0.092	BD
12/06	2520	1102	167	15.3	8.39	8.43	0.579	0.379	0.371	0.064	BD
19/06	2680	1158	173	15.6	8.39	8.46	0.610	0.468	0.376	0.329	BD

The direct reading instrumental results for conductivity, pH and TDS and the gravimetric analyses results for TDS and SS of the rinse solutions are presented in Tables 7.29 to 7.42. Measurements for the conductivity and pH of the solutions began from the start of the monitoring period (i.e. from the 13/02). Collection of samples for gravimetric analyses began on the 20/03, therefore there are no results for the first 5 weeks as indicated by NM (not measured) in Tables 7.29 to 7.42.

Table 7.29 Gravimetric measurements of TDS and SS and direct reading instrument measurements of TDS, conductivity and pH made on Tank 2

Date	Conductivity (µS/cm)	SS (mg/L)	TDS (g/L)		pH
			Gravimetric Analysis	Direct Reading Instrument	
13/02	622	NM	NM	NM	10.58
20/02	3190	NM	NM	NM	12.05
27/02	464	NM	NM	NM	11.14
06/03	1778	NM	NM	NM	11.78
13/03	2780	NM	NM	NM	11.87
20/03	4600	40.2	1.72	2.27	11.78
27/03	5410	43.9	1.97	2.62	11.70
03/04	2320	39.1	0.852	1.20	12.03
11/04	3120	37.6	1.18	1.61	11.98
17/04	3820	41.7	1.42	1.90	12.00
24/04	5450	38.3	2.23	2.68	11.80
09/05	888	32.3	0.365	0.48	11.42
15/05	3230	32.5	1.07	1.64	11.99
22/05	2050	43.5	0.805	1.06	11.86
29/05	1964	33.1	0.772	1.01	12.00
5/06	2470	8.4	0.900	1.23	12.00
12/06	1769	21.9	0.696	0.89	11.83
19/06	3320	32.4	1.23	1.62	11.87

Table 7.30 Gravimetric measurements of TDS and SS and direct reading instrument measurements of TDS, conductivity and pH made on Tank 4

Date	Conductivity (µS/cm)	SS (mg/L)	TDS (g/L)		pH
			Gravimetric Analysis	Direct Reading Instrument	
13/02	190	NM	NM	NM	9.37
20/02	296	NM	NM	NM	10.66
27/02	149	NM	NM	NM	9.80
06/03	287	NM	NM	NM	10.46
13/03	438	NM	NM	NM	10.70
20/03	367	0	0.191	0.18	10.30
27/03	461	9.8	0.232	0.23	10.72
03/04	262	0	0.143	0.13	10.40
11/04	232	0	0.117	0.11	10.24
17/04	644	1.12	0.343	0.33	10.71
24/04	523	4.9	0.285	0.29	10.35
09/05	188	0	0.108	0.10	9.90
15/05	249	0	0.127	0.13	10.30
22/05	331	0	0.182	0.17	10.49
29/05	189	0	0.108	0.09	10.24
5/06	179	0	0.0936	0.08	10.03
12/06	175	0	0.0798	0.08	10.40
19/06	306	0	0.168	0.14	10.04

Table 7.31 Gravimetric measurements of TDS and SS and direct reading instrument measurements of TDS, conductivity and pH made on Tank 5

Date	Conductivity (µS/cm)	SS (mg/L)	(TDS g/L)		pH
			Gravimetric Analysis	Direct Reading Instrument	
13/02	105	NM	NM	NM	7.83
20/02	107	NM	NM	NM	8.52
27/02	94	NM	NM	NM	7.50
06/03	114	NM	NM	NM	9.21
13/03	109	NM	NM	NM	8.90
20/03	109	0	0.0369	0.05	8.68
27/03	116	0	0.0627	0.05	9.12
03/04	100	0	0.0655	0.04	9.17
11/04	104	0	0.0580	0.05	8.65
17/04	135	0	0.0615	0.06	9.47
24/04	118	0	0.0416	0.06	8.70
09/05	93	0	0.0619	0.04	8.42
15/05	97	0	0.0522	0.05	8.84
22/05	104	0	0.0644	0.05	9.09
29/05	99	0	0.0698	0.05	8.71
5/06	102	0	0.0587	0.04	8.88
12/06	102	0	0.0478	0.04	9.09
19/06	104	0	0.0816	0.04	8.94

Table 7.32 Gravimetric measurements of TDS and SS and direct reading instrument measurements of TDS, conductivity and pH made on Tank 6

Date	Conductivity (µS/cm)	SS (mg/L)	TDS (g/L)		pH
			Gravimetric Analysis	Direct Reading Instrument	
13/02	102	NM	NM	NM	7.7
20/02	101	NM	NM	NM	8.25
27/02	89	NM	NM	NM	7.70
06/03	102	NM	NM	NM	8.52
13/03	98	NM	NM	NM	8.19
20/03	100	0	0.0562	0.05	7.94
27/03	103	0	0.0651	0.05	8.72
03/04	96	0	0.0629	0.04	8.89
11/04	100	0	0.0562	0.04	8.38
17/04	112	0	0.0633	0.05	9.03
24/04	98	0	0.0565	0.04	8.15
09/05	85	0	0.0494	0.04	8.44
15/05	90	0	0.0502	0.04	8.54
22/05	97	0	0.0475	0.04	8.88
29/05	97	0	0.0539	0.04	8.75
5/06	97	0	0.0594	0.04	8.65
12/06	98	0	0.0581	0.04	8.97
19/06	97	0	0.0615	0.04	7.46

Table 7.33 Gravimetric measurements of TDS and SS and direct reading instrument measurements of TDS, conductivity and pH made on Tank 8

Date	Conductivity (µS/cm)	SS (mg/L)	TDS (g/L)		pH
			Gravimetric Analysis	Direct Reading Instrument	
13/02	364	NM	NM	NM	4.78
20/02	236	NM	NM	NM	4.75
27/02	301	NM	NM	NM	3.94
06/03	232	NM	NM	NM	5.69
13/03	227	NM	NM	NM	4.68
20/03	368	0	0.167	0.19	3.66
27/03	953	0	0.380	0.53	2.97
03/04	617	0	0.243	0.32	3.46
11/04	570	0	0.243	0.31	3.42
17/04	778	0	0.309	0.42	3.04
24/04	2470	0	0.161	1.28	2.94
09/05	948	0	0.356	0.50	3.24
15/05	1244	0	0.467	0.64	3.10
22/05	1091	0	0.434	0.58	3.01
29/05	304	0	0.178	0.16	3.88
5/06	480	0	0.167	0.24	3.50
12/06	533	0	0.216	0.27	3.30
19/06	1195	0	0.448	0.59	3.43

Table 7.34 Gravimetric measurements of TDS and SS and direct reading instrument measurements of TDS, conductivity and pH made on Tank 9

Date	Conductivity (µS/cm)	SS (mg/L)	TDS (g/L)		pH
			Gravimetric Analysis	Direct Reading Instrument	
13/02	120	NM	NM	NM	7.44
20/02	103	NM	NM	NM	7.44
27/02	104	NM	NM	NM	7.47
06/03	103	NM	NM	NM	8.37
13/03	100	NM	NM	NM	7.94
20/03	110	0	0.0647	0.05	6.66
27/03	117	0	0.0638	0.05	6.39
03/04	110	0	0.0670	0.05	6.60
11/04	108	0	0.0665	0.05	8.27
17/04	122	0	0.0695	0.05	7.19
24/04	160	0	0.102	0.08	6.55
09/05	111	0	0.0400	0.05	7.07
15/05	121	0	0.0686	0.06	6.96
22/05	121	0	0.0797	0.06	7.14
29/05	102	0	0.0638	0.05	8.20
5/06	108	0	0.0558	0.05	7.58
12/06	112	0	0.0547	0.05	7.19
19/06	124	0	0.0916	0.05	7.45

Table 7.35 Gravimetric measurements of TDS and SS and direct reading instrument measurements of TDS, conductivity and pH made on Tank 12

Date	Conductivity (µS/cm)	SS (mg/L)	TDS (g/L)		pH
			Gravimetric Analysis	Direct Reading Instrument	
13/02	137	NM	NM	NM	7.95
20/02	122	NM	NM	NM	8.20
27/02	125	NM	NM	NM	7.40
06/03	150	NM	NM	NM	8.16
13/03	125	NM	NM	NM	7.96
20/03	153	0	0.111	0.07	7.50
27/03	144	0	0.111	0.07	7.97
03/04	102	0	0.0831	0.05	6.96
11/04	107	0	0.0680	0.05	8.02
17/04	169	0	0.138	0.08	8.01
24/04	146	0	0.176	0.07	7.89
09/05	92	0	0.111	0.05	8.24
15/05	172	0	0.178	0.09	8.00
22/05	188	0	0.177	0.09	8.11
29/05	116	0	0.109	0.05	8.38
5/06	115	0	0.0772	0.05	8.04
12/06	162	0	0.0796	0.07	7.77
19/06	183	0	0.135	0.08	8.14

Table 7.36 Gravimetric measurements of TDS and SS and direct reading instrument measurements of TDS, conductivity and pH made on Tank 13

Date	Conductivity (µS/cm)	SS (mg/L)	TDS (g/L)		pH
			Gravimetric Analysis	Direct Reading Instrument	
13/02	114	NM	NM	NM	8.01
20/02	125	NM	NM	NM	7.84
27/02	124	NM	NM	NM	7.35
06/03	123	NM	NM	NM	8.21
13/03	108	NM	NM	NM	7.85
20/03	139	0	0.120	0.07	7.62
27/03	124	0	0.104	0.06	6.21
03/04	116	0	0.0857	0.05	7.16
11/04	111	0	0.0808	0.05	8.14
17/04	164	0	0.106	0.07	8.10
24/04	133	0	0.100	0.06	7.95
09/05	91	0	0.0790	0.04	8.24
15/05	156	0	0.115	0.08	8.02
22/05	146	0	0.0983	0.07	8.12
29/05	131	0	0.0898	0.06	8.40
5/06	121	0	0.0642	0.05	8.37
12/06	145	0	0.0733	0.06	8.05
19/06	173	0	0.115	0.08	7.65

Table 7.37 Gravimetric measurements of TDS and SS and direct reading instrument measurements of TDS, conductivity and pH made on Tank 14

Date	Conductivity (µS/cm)	SS (mg/L)	TDS (g/L)		pH
			Gravimetric Analysis	Direct Reading Instrument	
13/02	101	NM	NM	NM	8.11
20/02	125	NM	NM	NM	6.93
27/02	105	NM	NM	NM	7.32
06/03	103	NM	NM	NM	8.75
13/03	99	NM	NM	NM	8.28
20/03	110	0	0.0686	0.05	7.59
27/03	100	0	0.0690	0.05	6.64
03/04	94	0	0.124	0.04	8.04
11/04	100	0	0.0519	0.04	8.73
17/04	143	0	0.0615	0.04	8.19
24/04	103	0	0.0663	0.05	8.19
09/05	88	0	0.0555	0.04	8.47
15/05	146	0	0.101	0.07	7.94
22/05	120	0	0.0785	0.05	8.10
29/05	98	0	0.0634	0.04	8.85
5/06	98	0	0.0465	0.04	8.70
12/06	112	0	0.0736	0.05	7.53
19/06	143	0	0.0999	0.06	8.25

Table 7.38 Gravimetric measurements of TDS and SS and direct reading instrument measurements of TDS, conductivity and pH made on Tank 16

Date	Conductivity (µS/cm)	SS (mg/L)	TDS (g/L)	pH
			Gravimetric Analysis	
13/02	84700	NM	NM	1.90
20/02	119700	NM	NM	0.90
27/02	123800	NM	NM	0.94
06/03	105400	NM	NM	0.90
13/03	101800	NM	NM	1.02
20/03	113800	25.1	39.36	1.42
27/03	109000	19.8	39.45	1.19
03/04	119800	13.8	39.15	1.16
11/04	98800	7.55	34.56	1.08
17/04	104600	88.9	37.63	0.71
24/04	121500	13.9	40.74	0.84
09/05	88800	6.8	29.98	1.14
15/05	97200	18.2	31.75	1.08
22/05	106400	55.9	35.80	0.75
29/05	84800	10.6	27.82	0.73
5/06	77200	16.9	24.62	0.84
12/06	74600	34.1	22.64	1.23
19/06	85900	21.1	26.41	1.22

Table 7.39 Gravimetric measurements of TDS and SS and direct reading instrument measurements of TDS, conductivity and pH made on Tank 18

Date	Conductivity (µS/cm)	SS (mg/L)	TDS (g/L)		pH
			Gravimetric Analysis	Direct Reading Instrument	
13/02	134	NM	NM	NM	7.21
20/02	171	NM	NM	NM	6.90
27/02	142	NM	NM	NM	7.22
06/03	**410**	NM	NM	NM	**3.72**
13/03	153	NM	NM	NM	6.79
20/03	191	0	0.101	0.10	6.11
27/03	161	0	0.103	0.08	7.28
03/04	120	0	0.0794	0.06	7.61
11/04	129	0	0.0791	0.06	7.24
17/04	148	4.78	0.101	0.07	6.94
24/04	204	29.7	0.138	0.11	6.46
09/05	100	0	0.0587	0.05	7.44
15/05	119	7.2	0.0952	0.06	7.30
22/05	150	20.5	0.0999	0.07	7.05
29/05	105	0	0.0713	0.05	7.90
5/06	155	5.4	0.100	0.07	6.85
12/06	127	0	0.0768	0.05	6.67
19/06	194	19.24	0.138	0.10	7.35

Table 7.40 Gravimetric measurements of TDS and SS and direct reading instrument measurements of TDS, conductivity and pH made on Tank 19

Date	Conductivity (µS/cm)	SS (mg/L)	TDS (g/L)		pH
			Gravimetric Analysis	Direct Reading Instrument	
13/02	132	NM	NM	NM	7.95
20/02	164	NM	NM	NM	7.52
27/02	146	NM	NM	NM	7.22
06/03	214	NM	NM	NM	6.50
13/03	130	NM	NM	NM	7.46
20/03	172	0	0.123	0.08	7.04
27/03	139	0	0.0843	0.07	7.30
03/04	192	0	0.111	0.10	7.40
11/04	229	4.27	0.144	0.11	8.39
17/04	225	6	0.128	0.11	7.27
24/04	144	0	0.0757	0.07	8.02
09/05	168	0	0.108	0.09	7.92
15/05	205	0	0.129	0.10	7.88
22/05	135	0	0.0849	0.06	8.34
29/05	197	0	0.112	0.10	8.40
5/06	256	3.2	0.145	0.12	7.88
12/06	104	0	0.0660	0.04	8.64
19/06	156	0	0.0907	0.07	7.69

Table 7.41 Gravimetric measurements of TDS and SS and direct reading instrument measurements of TDS, conductivity and pH made on Tank 20

Date	Conductivity (µS/cm)	SS (mg/L)	TDS (g/L)		pH
			Gravimetric Analysis	Direct Reading Instrument	
13/02	3150	NM	NM	NM	7.87
20/02	2740	NM	NM	NM	7.64
27/02	4280	NM	NM	NM	7.46
06/03	3560	NM	NM	NM	7.64
13/03	3760	NM	NM	NM	7.54
20/03	4200	1.33	6.19	1.93	7.34
27/03	4260	3.8	6.01	1.98	7.64
03/04	4270	8.5	6.24	1.95	7.74
11/04	3360	4.87	4.54	1.60	7.62
17/04	4140	4	4.69	1.62	7.56
24/04	3620	3.5	4.91	1.69	7.62
09/05	1955	0	2.35	0.97	7.71
15/05	2350	1.7	2.92	1.17	7.77
22/05	3340	6.8	4.45	1.53	7.65
29/05	3440	6.9	4.54	1.60	7.77
5/06	2320	3.4	2.82	1.09	7.87
12/06	2190	2.3	2.57	1.02	7.77
19/06	2260	0.5	2.73	1.02	7.96

Table 7.42 Gravimetric measurements of TDS and SS and direct reading instrument measurements of TDS, conductivity and pH made on Tank 21

Date	Conductivity (µS/cm)	SS (mg/L)	TDS (g/L)		pH
			Gravimetric Analysis	Direct Reading Instrument	
13/02	2730	NM	NM	NM	7.67
20/02	2210	NM	NM	NM	7.66
27/02	2340	NM	NM	NM	7.57
06/03	2150	NM	NM	NM	7.61
13/03	2730	NM	NM	NM	7.59
20/03	2760	6.76	4.05	1.34	7.39
27/03	2940	4.72	4.39	1.42	7.87
03/04	2740	5.12	3.90	1.32	7.75
11/04	2530	2.2	3.57	1.22	7.71
17/04	3480	6.84	6.29	1.86	7.64
24/04	6000	9.52	9.82	2.43	7.40
09/05	4270	253	6.83	1.83	7.54
15/05	4220	5.56	6.76	1.82	7.59
22/05	4860	20.6	8.43	1.98	7.53
29/05	5210	7.1	7.85	2.13	7.64
5/06	4530	6	7.11	1.83	7.63
12/06	4830	5.46	7.87	1.91	7.63
19/06	5090	5.24	7.43	1.98	7.71

7.4 New Data on Product Output

During each visit to the company, the production foreman of the Brass Division supplied the number and type of each workpiece treated on the CPL, during each sample period. These data together with the surface area calculated for each workpiece was used to determine the total surface area treated during each sample period.

Table 7.43 shows the estimated surface area of individual workpieces which have been processed on the CPL during each of the seventeen sample periods. The total surface area processed during each sample period is given in the last row of the table.

Table 7.43 Total surface area (m^2) of workpieces treated on the CPL

ork piece	Sample period															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
ıopy hinge	0.885	4.19		4.60							2.65	2.19				
ıopy hinge		0.381	0.572	5.09	8.90	1.91	2.29	1.27	3.81	21	1.65	3.18	1.91	2.25	8.24	
t hinge												0.427	0.421			
t hinge						0.241				0.241				0.048		
t hinge						0.227			0.809	1.12						
t hinge										0.102	0.307					
t hinge												0.193				
t hinge						0.359				0.575	0.596		0.050			
t hinge									1.04	1.04			0.948		0.717	
t hinge					0.270	4.32				4.32						
shered butt ge									3.42	3.42						
kless hinge			3.29				5.17			5.17				0.949		
kless hinge		4.01								4.66		1.24		1.46	2.33	
kless hinge				0.628					1.14	1.14						
ıdow hinge						0.473				0.473			0.473	0.473		
liament ge													0.186	0.186		
liament ge	0.354						0.172			0.172					0.478	
liament ge									0.359	0.530						
liament ge						0.225				0.188						
jection ge						1.46				1.46						
jection ge										2.36						
p & Staple									2.06	2.06	0.597					
p & Staple									2.36	3.92	1.48	0.296	2.96			

Table 7.43 Total surface area (m^2) of workpieces treated on the CPL continued

ork piece	Sample period															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
p & Staple					2.57											
rel bolt	0.916	3.87		2.54	0.763		3.64			3.64			2.72	2.57		
rel bolt	9.86	0.837	1.82		9.86	16.0			5.60	24.9	3.64					
rel bolt	5.89	1.92					5.01			5.01						
rel bolt			3.83													
rel bolt			1.18													
rel bolt			2.27													
k bolt				1.22	0.166		2.60	0.332		2.93						
k bolt			2.583													
k bolt				7.26	11		1.31			3.56	4.36		5.56			
k bolt					0.468	4.68			0.047	4.72						
k bolt			4.09								1.64					
er flush t													0.130			
er flush t					0.281					0.175						
utcheon		0.043							0.023	0.023						
utcheon					0.067											
light stays	0.203															
h fastener ch				0.485												
h window			0.343	0.318	1.59	1.47				2.21			2.05	0.491		
vy duty ng clip	1.05	1.91		10.8	2.70					0.051		1.11			0.953	
ement dles		7.19	4.49			9.57				9.57				7.07		
ement dles				4.60			13.2	3.78		19.8				11.3		
ace area luring SP	**19.2**	**24.4**	**24.5**	**32.9**	**38.6**	**40.9**	**33.4**	**5.38**	**20.7**	**131**	**16.9**	**8.64**	**17.4**	**26.8**	**12.7**	

CHAPTER 8

DISCUSSION

A waste minimisation audit was carried out on the Chromium Plating Line (CPL) at Howick Metal Products from 13th February to 19th June 2007. The CPL pre-treats, plates and post-treats a variety of small work pieces (door and window fittings). The audit data will be used to identify and quantify waste minimisation opportunities in the CPL.

In Sections 8.1 and 8.2 respectively the analytical results of the process and rinse solutions are discussed. These sections include an estimation of the extent of chemical additions made into the process solutions and the rinse solution dumping frequency. In Section 8.3 a mass balance analysis is performed on the water usage, involving a breakdown of the water usage in both the Brass Division and the CPL. The determination of drag-out volumes using elemental analysis is carried out in Section 8.4. The construction of the CPL is such that, the gutter that collects all the waste and discharges it into the sewer, is not accessible for sampling. Therefore in Section 8.5 estimates are made of the effluent stream concentration and in Section 8.6, the true cost of waste analysis is carried out. Section 8.7 describes the monitoring and targeting analysis carried out using the consumption variable (water) and the production variable (surface area treated).

Table 8.1 summarises the sampling frequency used in this study which will be referred to in this discussion on the water usage, solution chemistry and waste minimisation analysis. The start of the sample period (SP) is when monitoring of the CPL was carried out on a Tuesday. The beginning of the sample period is therefore on the Tuesday and the end of the sample period is five working days later on the Monday before the next sampling day. The number of days between the sample periods and the number of hours the CPL was in operation is shown in Table 8.1.

Table 8.1 Breakdown of the monitoring period into sample periods and operating hours

Sample period (SP)	Date at the beginning of sample period	Date at the end of sample period	CPL operating hours	No. of working days
1	13/02	19/02	37.5	5
2	20/02	26/02	37.5	5
3	27/02	5/03	37.5	5
4	6/03	12/03	37.5	5
5	13/03	19/03	37.5	5
6	20/03	26/03	30	4
7	27/03	2/04	37.5	5
8	3/04	10/04	22.5	3
9	11/04	16/04	37.5	5
10	17/04	23/04	37.5	5
11	24/04	7/05	67.5	9
12	8/05	14/05	30	4
13	15/05	21/05	37.5	5
14	22/05	28/05	37.5	5
15	29/05	4/06	37.5	5
16	5/06	11/06	37.5	5
17	12/06	19/06	37.5	5

8.1 Characterisation of Process Solutions

Chemical additions are made into the process tanks in order to maintain a constant concentration level in the process solution. The process tanks operate at their best when their concentrations are maintained within the specified levels. During the waste minimisation audit, the line supervisor indicated that occasionally random chemical additions were made into the process tanks. These additions are not documented on the Analysis Reports as they are not suggested by the supplier. Every effort was made to obtain accurate information about the date and quantity of these additions made during the monitoring period. The line operators were given a calendar to place on the wall close to the CPL. Whenever any additions or dumping occurred on the CPL, they were asked to record the date and all details. However this was only partially successful as the chemical additions made were occasionally recorded but the quantities were not, and since this was not a routine procedure, they may have occasionally forgotten to record the information.

Chemical analysis was conducted on the process solutions in the CPL, to produce concentration profiles of the process tanks for the full monitoring period. The concentration profiles were used to monitor the concentrations of the key elements in the process solutions. The concentration profiles were therefore used to cross-check to determine if the chemical additions recorded on the Analysis Reports and by the line operators were actually carried out and if any additions were made into the process tanks that were not recorded.

Figure 8.1 shows how the concentration profiles in the electrocleaner, Tank 3 (see Table 7.8), were used to determine if chemical additions were made into the tank.

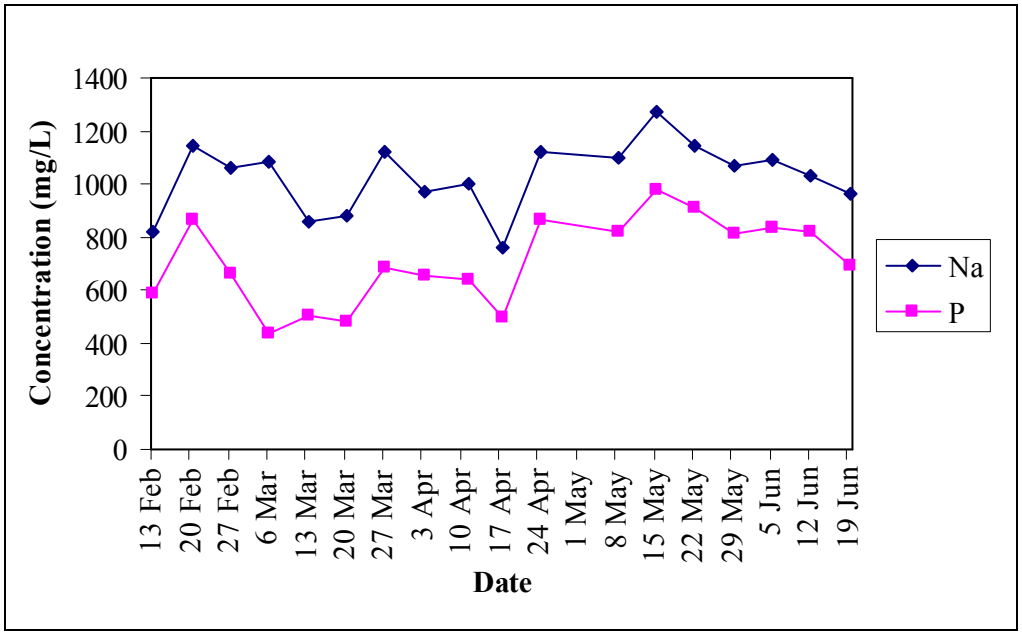

Figure 8.1 Concentration profile of Tank 3

The Analysis Reports from the chemical supplier, indicate that chemical additions were made to the electrocleaner (Tank 3) on 16/02 and 14/06. On the 16/02 1.8 kg of Orprep HP16 was added to the tank. This is reflected by an increase in Na and P concentration between the 13/02 and the 19/02 (SP 1). However, although the Analysis Report recommended that 0.8 kg Orprep HP16 should be added on the 14/06, chemical analysis

shows a decrease in Na and P concentration between 12/06 and 19/06 (SP 17). Thus it is doubtful that the addition was actually made.

An addition on the 15/05 was documented by the line operators, however the quantity added was not recorded. This addition is reflected by the increase in Na and P between the 8/05 and 14/05 (SP 12).

According to Figure 8.1, there were also significant increases in Na and P concentrations during the 20/03 to 26/03 (SP 6) and 17/04 to 23/04 (SP10). However there were no records kept of any additions made during this time. It is therefore possible that two more additions were made into the tank during SP 6 and SP 10 that were not recorded.

The concentration profiles for the other process tanks (Tanks 1, 7, 10, 11, 15 and 17) are given in Appendix A. The concentration profiles show that there is no systematic procedure to record important information on the CPL. Unrecorded additions to the tanks appear to have been made, and it is doubtful that certain additions documented on the Analysis Reports were made. There is no record kept of the quantity of chemicals used and the amount still in stock. The company therefore needs to implement more control over their chemical use and stock control by keeping a proper record of all chemicals used on the CPL. This information is also important in a waste minimisation audit as it can be used in a scoping audit to help identify potential areas for waste minimisation opportunities

8.2 Characterisation of Rinse Solutions

Rinse solutions become contaminated with drag-out from the process solutions which contains chemicals, by-products and impurities. The rinse tanks are therefore occasionally dumped and refilled with clean water to prevent the build up of contaminants in the rinse solutions, which would be harmful to the workpiece surface. The company, however, does not keep any records indicating the date when dumping occurs, the tanks which are dumped, or the volume of rinse water dumped from the CPL.

The estimation of the frequency of dumping of rinse solutions is important in a waste minimisation audit as it is used to determine the water usage of the rinse tanks on the CPL. Knowledge of the water usage in the rinse tanks on the CPL is important as it is used in the mass balance analysis of water in Section 8.3. The 10 flowing rinses (Tanks 2, 4-6, 8-9, 12-14 and 18) are continually being refreshed with clean water. Measurements of average flow of water were regularly made (see Table 7.16) to account for the water usage through the flowing rinse tanks. However we have been informed by the line operators that these tanks are occasionally dumped and refilled with clean water. Thus the actual water usage was greater than that calculated from the constant flow. Since there were no records kept of the dates on which dumping of the rinse tanks occurred, there was a need to find a way to determine, from empirical evidence, when the tanks were dumped. It was considered that elemental analysis and measurements of conductivity and TDS would be able to indicate when the tanks were dumped. A sudden decrease in concentration, conductivity and TDS between consecutive readings would indicate that the tank contents had been replaced by clean water.

The following method was used to determine when the tanks were being dumped and recharged. The conductivity, TDS and concentration measurements show a gradual increase, followed by a sharp drop in the respective measurements at dumping (this pattern is illustrated in Figure 8.2). It is then assumed that the tanks were dumped and recharged in the sample period between the highest and lowest conductivity, TDS and concentration values. (However since TDS analysis began on the 20/03, these

measurements can only be used from SP 6 to verify the dumping and recharging of rinse tanks.)

Figure 8.2 looks at the soak cleaner rinse, Tank 2, and illustrates how the elemental concentrations, conductivity and TDS results (see Table 7.29) were used to determine dumping times.

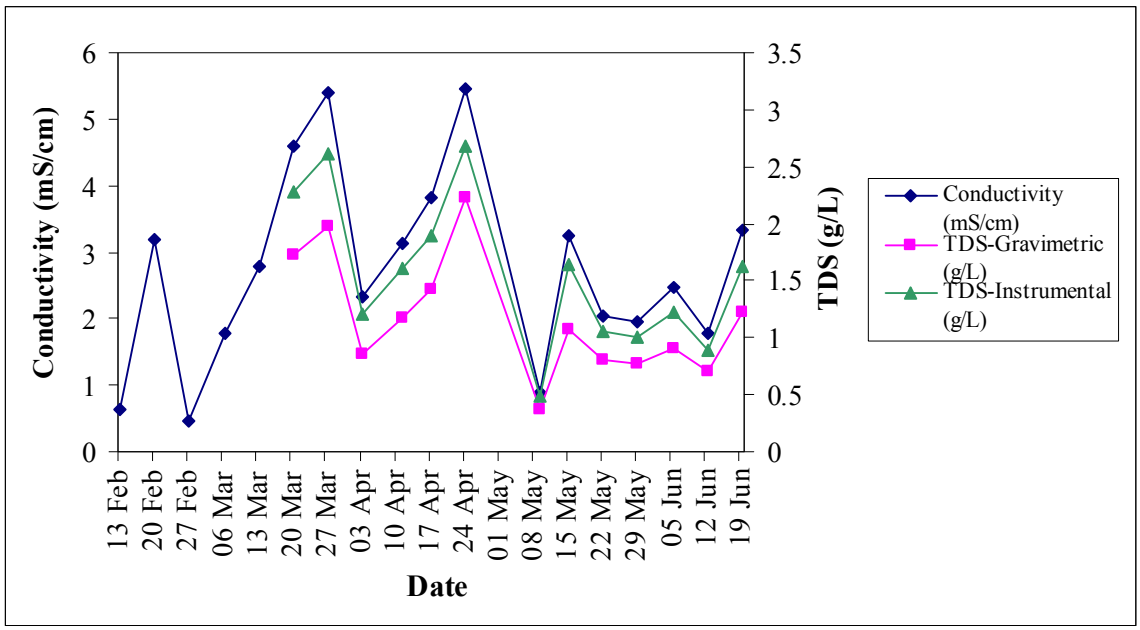

Figure 8.2 Conductivity and TDS profile for Tank 2

The dumping times were estimated using the following approach. Between the 20/02 and 26/02 (SP 2) there is a sharp drop in conductivity from 3.19 to 0.464 mS/cm (see Figure 8.2) therefore dumping must have occurred during this time. Similarly between the 27/03 to 2/04 (SP 7) and the 24/04 to 7/05 (SP 11) there is gradual increase in concentration followed by a sharp drop in the conductivity and TDS readings. It is therefore taken that dumping occurred during these sample periods. There is a lot of uncertainty with whether the drop in conductivity and TDS during the 15/05 to 21/05 (SP 13) and the 5/06 to 11/06 (SP 16) represent dumping as the peaks are not as sharp as the other drops. However the conductivity and TDS did not increase significantly during this time even though a normal throughput of workpieces was maintained, therefore it is assumed dumping occurred during SP 13 and SP 16. This indicates that the company is dumping their rinse tanks too soon i.e. when the concentration in the tank is still low.

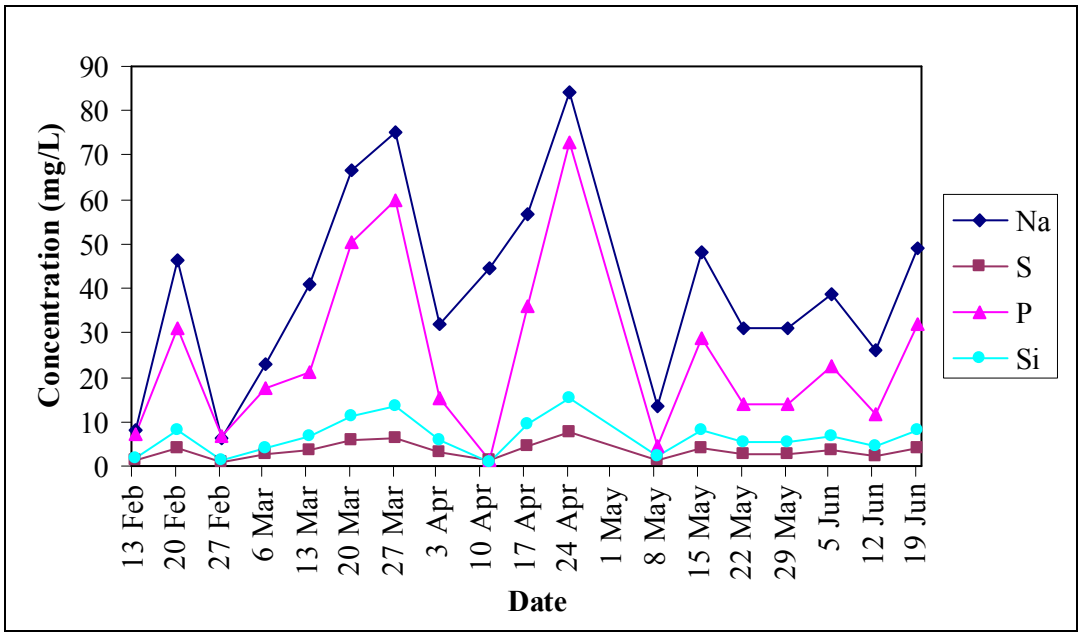

Figure 8.3 Concentration profile of Tank 2

A similar pattern is seen in Figure 8.3 when using elemental concentrations (see Table 7.15). The peaks indicative of dumping show a gradual increase in concentration (for example from the 27/02 to 27/03) followed by a sharp drop in concentration (between the 27/03 and 3/04). The sharp drop in elemental concentrations during the 20/02 to 26/02 (SP 2), 27/03 to 2/04 (SP 7) and 24/04 to 7/05 (SP 11) are therefore indicative of dumping and recharging the tank. The drop in concentration between the 15/05 and 21/05 (SP 13) and 5/06 and 11/06 (SP 16) is not very steep, however since the concentration did not increase during this time, it is therefore assumed that dumping occurred during these sample periods. These peaks are analogous to the peaks present on the conductivity/TDS profile (see Figure 8.2).

The conductivity/TDS and concentration profiles for Tank 2 (Figures 8.2 and 8.3) show that the dumping patterns are the same in both graphs, therefore the inferences made on estimating dumping times were the same using both profiles. The concentration and conductivity/TDS profiles for the other rinse tanks (Tanks 4, 5, 6, 8, 9, 12, 13, 14, 18 and 19) are shown in Appendix B. The dumping frequencies for the other rinse tanks were

made using the same approach described above for rinse Tank 2. The dumping frequency for the rinse tanks on the CPL were estimated and are presented in Table 8.2.

Table 8.2 Dumping of rinse tanks based on empirical evidence

Sample period	Rinse tanks dumped	Volumes dumped (L)
1	No dumping	0
2	2,4,5 and 6	460
3	No dumping	0
4	12,13,14,18,19	618
5	No dumping	0
6	19	200
7	2,4,5,6,8,9,12,13,14 and18	1138
8	No dumping	0
9	No dumping	0
10	19	200
11	2,4,5,6,8,9,12,13,14 and 18	1138
12	No dumping	0
13	2 and 19	300
14	4,5,6,8,9,12,13,14 and 18	1038
15	No dumping	0
16	2 and 19	300
17	No dumping	0
	Total water dumped	**5392**

The elemental analysis can be used as an indicator of when to dump the rinse tanks. However elemental concentrations are obtained through ICP-OES analysis. This means that the samples need to be collected and taken to a lab for analysis, which is both time-consuming and expensive. The comparison between concentration and conductivity show that the latter can also be used to establish dumping times successfully. Therefore the conductivity results can be used to estimate dumping frequency. The advantages with taking conductivity measurements are that they can be taken on-site, the results are obtained instantly and it is very cheap, quick and easy.

The concentration and conductivity profiles, illustrate that there is no clear pattern of when the company decides to dump the rinse tanks. On certain occasions the concentration is left to increase and then the tanks are dumped and other times the

concentration does not reach a very high level yet the tanks are still dumped. The company can therefore measure the conductivity of the rinse tanks and use the conductivity profiles as an indicator of when the tanks require dumping. When the conductivity reaches a specific target value they should dump and refill the tanks. This offers two advantages, it prevents the wastage of water incurred by dumping and refilling the tanks with fresh water too quickly and it also prevents the build-up of contaminants by preventing the elemental concentrations from reaching high levels in the tank which would be damaging to the workpieces.

8.2.1 TDS and Conductivity Measurements

It is expected that the conductivity and the TDS will be strongly correlated since the dissolved solids are largely salts which also contribute to the conductivity of the solution. The conductivity and TDS using a direct reading instrument show a good correlation and this is expected as the TDS measurements are based on the conductivity of the solution (i.e. both these measurements are based on the total ions present in the solution).

The ratio of TDS (gravimetric)/conductivity was calculated for each rinse tank to give a factor (see Table 8.3). This factor was relatively constant for each tank and the average values are given below. Different tanks have different factors, since the tanks have different compositions and the TDS/conductivity ratio depends on the chemical composition of the tank. This factor is beneficial as it allows the TDS (gravimetric) values to be estimated. Since gravimetric analysis is time consuming this would provide a quick and simple method for calculating the TDS concentrations.

Table 8.3 TDS/Conductivity factors for the rinse tanks

Tank	Tank No.	TDS/Conductivity factor (g cm/ L mS)
Soak cleaner rinse	2	0.38
Electrocleaner rinse	4	0.53
	5	0.56
	6	0.58
Galtin rinse	8	0.38
	9	0.58
Nickel rinse	12	0.85
	13	0.71
	14	0.67
Neutralizer rinse	18	0.65
Hot water rinse	19	0.60

The TDS values are beneficial as they can be used to determine if the flow rates of the flowing rinses are set at an acceptable rate. The TDS values in Table 8.4 were cited in literature[81] and give the acceptable concentration range when the rinsing flow rates are adequate. If the TDS values are within the range shown in Table 8.4, the rinse water flow rates are appropriate, if the values are too low then the flow rates may be too high resulting in the wastage of water and therefore needs to be adjusted to a lower rate. If the contaminant values are high then the rinse flow needs to be changed to a higher rate. However if the TDS values are significantly higher than the maximum value in the range, than the contaminant level in the tank is too high and the contents of the tank need to be dumped. The company can therefore measure the conductivity and use Table 8.4, to determine if contaminants are within reasonable limits and if the flow rates are satisfactory.

Table 8.4 Rinse criteria for permissible levels of contamination[81]

Type of rinse	Normal range for adequate rinsing (TDS, mg/L)
Following cleaner/acid pickle	400 to 1000
Following functional plating	100 to 700
Following bright plating	5 to 40

For a counter-current rinse system the values in Table 8.4 are compared to the concentration in the cleanest rinse (i.e. least contaminated rinse). The TDS results for the flowing rinses (see Table 8.5) on the CPL were compared to the values in Table 8.4. Rinse Tanks 2, 4 and 9 follow the cleaner/acid pickle (i.e. 400 to 1000 mg/L in Table 8.4) and rinse Tank 14 follows the bright plating (i.e. 5 to 40 mg/L in Table 8.4). The results show that on certain occasions the contaminant level in the soak cleaner rinse (Tank 2) was quite high, this implies that the rinse flow should be adjusted to a higher rate. The TDS values for the electrocleaner (Tank 6) and the Galtin rinses (Tank 9) are much lower than the minimum of 400 mg/L from Table 8.4. This suggests that the flow rates used are too high and need to be changed to a lower rate as these tanks do not require such thorough rinsing. The contaminant level in the nickel rinse is higher than the range of 10 to 40 mg/L given in Table 8.4, the flow rate is possibly set too low and needs to be adjusted to a higher rate.

Table 8.5 TDS (mg/L) values for the flowing rinses on the CPL

Date	Tank 2 (soak cleaner rinse)	Tank 6 (electrocleaner rinse)	Tank 9 (Galtin rinse)	Tank 14 (nickel rinse)
20/03	1720	56.2	64.7	68.6
27/03	1970	65.1	63.8	69
03/04	852	62.9	67	124
11/04	1180	56.2	66.5	51.9
17/04	1420	63.3	69.5	61.5
24/04	2230	56.5	102	66.3
09/05	365	49.4	40	55.5
15/05	1070	50.2	68.6	101
22/05	805	47.5	79.7	78.5
29/05	772	53.9	63.8	63.4
5/06	900	59.4	55.8	46.5
12/06	696	58.1	54.7	73.6
19/06	1230	61.5	91.6	99.9

8.3 Water Balance Analysis

The data used for the water balance analysis, was the existing (historic) and new (live) data. The existing data is the Umgeni Municipality Tax Invoice which includes the volume and cost of water used by the whole Brass Division. This water consumption includes water used on the CPL, water used in the ablution block, water used for gardening and by other departments (see Equation 8.1). The new data used is the rinse water flow rates and dumping frequencies.

$$MW = CPL + D + G + O \qquad \textit{Equation 8. 1}$$

Where MW = Umgeni Municipality Tax Invoice for water meter. Incoming water to the brass section

CPL = Water used on the CPL

D = Volume of water used in the ablution block

O = Volume of water used in other departments in the brass section

G = Volume of water used in gardening

The total water usage on the CPL was calculated using Equation 8.2

$$CPL = SR + FR + P + AP + ASR + E \qquad \textit{Equation 8.2}$$

Where SR = Volume of static rinse water (see Section 8.3.1.3)

FR = Volume of flowing rinse water (see Section 8.3.1.1)

P = Volume of water in process solution (see Section 8.3.1.2)

AP = Volume of water additions to process solutions (see Section 8.3.1.2)

E = Volume of water evaporated from solutions (see Section 8.3.1.4)

ASR= Volume of water additions to static rinse (see Section 8.3.1.3)

Section 8.3.1 involves a breakdown of the water usage to determine the various uses of water on the CPL and for non-CPL activities in the Brass Division. In Section 8.3.2 the water usage projected from the Umgeni Municipality water bills is compared to the total water usage estimated in Section 8.3.1.

8.3.1 Breakdown of water usage

Water is an important commodity in any chromium plating line. In the CPL water is used in all 21 tanks (7 process and 14 rinse tanks). Water is used in these tanks for running the countercurrent flowing rinse tanks (4-6, 8-9 and 12-14), in the flowing and static rinse tanks (2, 18 and 19) and in the process solutions (Tanks 1, 3, 7, 10, 11, 15 and 17). Water is used as a solvent in the process tanks in order to dissolve the treatment chemicals. When the water in these tanks becomes contaminated and the process solutions and rinse waters become exhausted they are dumped and refilled. The contaminants come from the chemicals in the raw materials, impurities in the raw materials, drag-out, by-products and the dirt removed from the surface of the workpieces. Water additions are also made to replace water lost by evaporation from hot process solutions and rinses and drag-out losses from the process and rinse tanks.

There is no water meter attached to the pipe taking water into the CPL. There are no water meters on the individual taps supplying water to the flowing rinse tanks. The total amount and distribution of the water in the CPL between process and rinse solutions within a year were based on the following assumptions:

- The solution volumes in the tanks were assumed to be the volume of the individual tanks or the volume quoted by the chemical supplier. The process and rinse solutions are assumed to contain this volume on dumping.
- Water flow rates entering and leaving the CPL were assumed to be equal.
- Water flow rates were measured at the start of each sample period (Tuesday) and these are assumed constant for entire sample period.

- Because dumping and recharging of the rinse tank solutions were not routinely documented the dumping dates had to be estimated using concentration and conductivity data. The frequency of dumping is estimated in Section 8.2.
- Water additions used to replace water loss due to drag-out and evaporation in the process solutions were made using Equation 8.3.

$$\text{Volume of solution added (L)} = \frac{\text{Mass of chemicals added (g)}}{\text{Specified concentration (g/L)}} \quad \textit{Equation 8.3}$$

The specified concentration in Equation 8.3 is equivalent to the make-up concentration established during charging the tank with the commercial (cleaning and plating) product. The make-up concentration was obtained from the Artek Analysis Report. The concentration was quoted as the number of grams of ingredient which must be present in the volume of the processing solution used in the tank. The volume of solution added is assumed to be the volume of water added to the process tanks.

- The CPL worked effectively for 37.5 hours from Monday to Friday. The total working days on the CPL in the year of 2007 were 238.
- Water usage is calculated based on the monitoring period of 85 days and converted to an annual figure (238 days).
- During the monitoring period the process solutions were not dumped, they were only topped up.
- All process solutions except the nickel and chromium baths, and all rinse tanks except the nickel and chromium drag-out tanks are dumped once a year, during the annual shutdown period.
- Effluent samples were unobtainable but the concentration of the effluent has been estimated for each sample period based on the water throughput on the line during the sample period and an average of the concentration measurements taken at the beginning of successive sample periods (see Section 8.5.).

8.3.1.1 Estimation of the Water Consumption by Flowing Rinses on the CPL

Both forms of rinsing used are used on the CPL namely static and flowing. In the case of flowing rinses there is a continuous flow of clean mains water into the rinse tanks and an outflow of dirty rinse water (wastewater or effluent) from the tank into the gutter and out to the drain. The water flow rates for each of the flowing rinse systems were calculated using Equation 8.4.

$$\text{Rinse water flowrate (L/min)} = \frac{\text{Volume of flowing rinse water (L)}}{\text{Time elapsed (min)}} \qquad \textit{Equation 8.4}$$

The water usage of the flowing rinses for each sample period was calculated using Equation 8.5 below.

$$\text{Water used in flowing rinses (L)} = \text{Operating time (min)} \times \text{Flow rate (L/min)} \qquad \textit{Equation 8.5}$$

Table 8.6 Rinse tank volume, flow rate, operating time and water used during the respective sample period

Sample Period	Tank	Flow rate (L/min)	Solution volume (L)	Operating time (min)	Water used (kL)
1	2	0.92	100	2250	2.070
	6	0.72	120		1.620
	9	0.39	130		0.878
	14	0.35	110		0.788
	18	0.39	88		0.878
2	2	0.65	100	2250	1.463
	6	1.00	120		2.250
	9	1.16	130		2.610
	14	2.76	110		6.210
	18	1.60	88		3.600
3	2	1.89	100	2250	4.253
	6	1.50	120		3.375
	9	0.34	130		0.765
	14	1.33	110		2.993
	18	3.00	88		6.750
4	2	0.82	100	2250	1.845
	6	0.95	120		2.138
	9	0.82	130		1.845
	14	1.29	110		2.903
	18	1.33	88		2.993
5	2	0.4	100	2250	0.900
	6	0.4	120		0.900
	9	0.75	130		1.688
	14	1.33	110		2.993
	18	4.0	88		9.000
6	2	0.92	100	1800	1.656
	6	0.21	120		0.378
	9	0.11	130		0.198
	14	0.58	110		1.044
	18	1.38	88		2.484

Table 8.6 Rinse tank volume, flow rate, operating time and water used during the respective sample period Continued

Sample Period	Tank	Flow rate (L/min)	Solution volume (L)	Operating time (min)	Water used (kL)
7	2	0.75	100	2250	1.688
	6	1.57	120		3.533
	9	0.24	130		0.540
	14	0.63	110		1.418
	18	0.12	88		0.270
8	2	1.44	100	1350	1.944
	6	0.95	120		1.283
	9	0.13	130		0.176
	14	0.25	110		0.338
	18	0.19	88		0.257
9	2	2.77	100	2250	6.233
	6	0.84	120		1.890
	9	Tap closed	130		0.000
	14	0.35	110		0.788
	18	0.25	88		0.563
10	2	2.25	100	2250	5.063
	6	0.5	120		1.125
	9	0.35	130		0.788
	14	0.21	110		0.473
	18	0.38	88		0.855
11	2	0.63	100	4050	2.552
	6	0.75	120		3.038
	9	Tap closed	130		0.000
	14	0.92	110		3.726
	18	Tap closed	88		0.000
12	2	4.5	100	1800	8.100
	6	2.25	120		4.050
	9	0.20	130		0.360
	14	0.34	110		0.612
	18	0.86	88		1.548

Table 8.6 Rinse tank volume, flow rate, operating time and water used during the respective sample period Continued

Sample Period	Tank	Flow rate (L/min)	Solution volume (L)	Operating time (min)	Water used (kL)
13	2	3.6	100	2250	8.100
	6	0.86	120		1.935
	9	0.18	130		0.405
	14	1.2	110		2.700
	18	0.29	88		0.653
14	2	1.50	100	2250	3.375
	6	0.46	120		1.035
	9	0.10	130		0.225
	14	0.46	110		1.035
	18	0.38	88		0.855
15	2	4.50	100	2250	10.125
	6	0.60	120		1.350
	9	0.71	130		1.598
	14	0.19	110		0.428
	18	0.75	88		1.688
16	2	1.64	100	2250	3.690
	6	1.16	120		2.610
	9	0.18	130		0.405
	14	1.71	110		3.848
	18	0.12	88		0.270
17	2	2.57	100	2250	5.783
	6	0.50	120		1.125
	9	0.38	130		0.855
	14	1.44	110		3.240
	18	0.32	88		0.720
	Total volume of water used for 85 days (kL)				**185**
	Total volume of water used for 238 days (kL)				**517**

The volume of water used to refill the rinse tanks after dumping is given in Table 8.7. The dumping frequencies were estimated in Section 8.2. The flowing tanks are discarded once a year during the annual shut down period. The volume of water used to refill the tanks after this dumping is shown in Table 8.8.

Table 8.7 Annual volume of water used to refill flowing rinse tanks after dumping

Sample period	Rinse tanks dumped	Volume of water used to refill tanks (kL)
2	2,4,5 and 6	0.460
4	12,13,14 and18	0.418
7	2,4,5,6,8,9,12,13,14 and18	1.138
11	2,4,5,6,8,9,12,13,14 and 18	1.138
13	2	0.100
14	4,5,6,8,9,12,13,14 and 18	1.038
16	2	0.100
Total volume of water used for 85 days		**4.392**
Total volume of water used for 238 days		**12.30**

Table 8.8 Volume of water used to refill flowing rinse tanks after annual dumping during the shut down period

Tank	Volume (kL)
2	0.100
4, 5 and 6	0.360
8 and 9	0.260
12, 13 and 14	0.330
18	0.088
Total volume used for refilling tanks	**1.138**

8.3.1.2 Estimation of the Water Consumption through topping Process Solutions on the CPL

Water is used as the solvent to prepare the chemicals for the process solutions. The process solutions operate with the chemicals set within a specific concentration range and this is set by the supplier. However chemicals and water are lost due to surface treatment reactions, drag-out and evaporation therefore chemical and water additions are made to the process solutions to restore the concentrations to the specified level. The supplier monitors the tanks regularly and determines if chemical additions are required. These

chemical additions are recorded on the Analysis Report whereas the volume of water added is not. The amount of water added to the process solutions is estimated using Equation 8.3 if the chemical additions are known and the concentration of the process solution is maintained within the specified level. The volume of water additions made to the process solutions is given in Table 8.9.

$$\text{Volume of solution added (L)} = \frac{\text{Mass of chemicals added (g)}}{\text{Specified concentration (g/L)}} \qquad \textit{Equation 8.3}$$

Table 8.9 Estimation of the volume of water additions made into the process solutions during the full monitoring period

Date	Tank	Chemical	Specified Conc. (g/L)	Chemical Addition	Water Equivalent (kL)
16/02	1	HP 100	75	2.6 kg	0.035
	3	HP 16	50	1.8 kg	0.036
	10	$NiSO_4$	300	17 kg	0.057
		$NiCl_2$	65	1 kg	0.015
	15	Lumina 34	300	17 kg	0.057
11/04	10	Magnum 821	6	285 g	0.048
	11	Magnum 821	6	912 g	0.152
14/06	3	HP 16	50	0.8 kg	0.016
	7	Dry acid salts	22	1.2 kg	0.018
	10	NiSO4	300	9 kg	0.03
		NiCl2	65	3.3 kg	0.051
		Boric acid	45	3.3 kg	0.073
		Magnum 821	6	912 g	0.152
		Leveller	30	10 kg	0.333
	15	Lumina 34	300	4.2 kg	0.014
				Total	**1.087**

The cleaning and neutralizer process solution (Tank 1, 3, 7 and 17)) are dumped at the end of each year and made up fresh at the beginning of the new working year. The amount of water required to make up the new solutions are given in Table 8.10.

Table 8.10 Volume of water used to make up fresh process solution

Tank	Volume of water (kL)
1	0.095
3	0.100
7	0.180
17	0.190
Total water used to refill process tanks	**0.565**

8.3.1.3 Water Used in Static Rinse Tanks on the CPL

Static rinse tanks are non-flowing rinses, they do not have an inflow or outflow of water. The total volume of water used in the static rinse tank (Tank 19) was estimated by using the volume of the rinse solution and the number of dumps of the solution (Equation 8.6). The frequency of dumping observed during the monitoring period was 5, this was converted to an annual figure of 14. The static rinse tank is also dumped at the end of the year during the annual shut down period to give a total of 15 dumps per year.

Total Volume of Rinse Water	=	Volume of Static Solution	x	Frequency of dumping	*Equation* 8.6

Table 8.11 Volume of water used for static rinse tank

Tank	Volume of Tank (kL)	Number of dumps per year
19	0.200	15
Volume of water used to refill after dumping (kL)		**3.0**

8.3.1.4 Water Used in the Drag-out Tanks on the CPL

Drag-out tanks are static tanks that usually follow the plating baths. They are used to wash the workpieces after plating and prior to the flowing rinse system, thereby reducing the carry-over of process solution to the subsequent flowing rinses. The chromium and nickel drag-out tanks (Tanks 16, 20 and 21) were excluded from estimating dumping dates as these solutions are not dumped. They are used to top up the chromium and nickel baths, to replace chemicals lost due to drag-out and evaporation.

Table 8.12 Annual volume of water used in drag-out tanks

Tank	Volume of the drag-out tank (L)	Volume of drag-out added to the process bath per day (L)	Volume of drag-out added to process baths per year (kL)
20	190	15	3.570
21	230	15	3.570
16	190	15	3.570
Total volume of water used in drag-out tanks (kL)			**10.71**

8.3.1.5 Estimation of the Water Consumption by non-CPL activities in the Brass Division

Water is not only used on the CPL in the Brass Division but also in other domestic functions. Domestic uses include water used in toilets, showers and gardening. The volume of water used in toilets was estimated to be 9 L/flush[86,125] and an average of three toilet visits per person (Brass Division only) per day. The volume of water used in the shower facility was estimated at 14 L/min.[86] Only 4 workers in the brass division take a shower once in the morning for an average of 5 minutes. The factory has a small garden that is watered three times a week. The water used is from the Brass Division. The volume of water used for hosing the garden was estimated at 1200 L/hour.[86] Water used for refreshment purposes was also calculated. An estimated 1 cup of tea per day (approximately 500 mL per cup) was consumed by each worker. The Brass Division has 85 workers and operates for a total of 238 days a year. Therefore the volume of water used annually was estimated using these values and the relevant rate for each activity.

Table 8.13 Volume of water used by non-CPL activities

	Annual Volume (kL/year)
Toilets	546
Showers	67
Gardening	122
Refreshments	10.1

8.3.2 Total Water Usage

The basic water rate of R 7.15 per kL was used to calculate the cost of water usage shown in Table 8.14. Data from Tables 8.6 to 8.13 were used for Table 8.14.

Table 8.14 Estimation of total water usage in Brass Division

	Annual Volume (kL/year)	Cost (R)	% of the total
Refilling the process tanks	0.565	4.04	0.044
Refilling the flowing rinse tanks	1.138	8.14	0.088
Refilling the static rinse	0.200	1.43	0.015
Water addition to the process solutions	1.087	7.77	0.084
Water additions to the static rinse	2.8	20.0	0.22
Water additions to flowing rinses	12.30	87.9	0.95
Water additions to drag-out	10.71	76.6	0.83
Flowing rinse water	517	3697	40
Toilets	546	3904	42
Showers	67	479	5.2
Gardening	122	872	9.5
Refreshments	10.1	72.2	0.78
Total	**1291**	**9230**	

The average volume of water used in the Brass Division was estimated to be 1291 kL. This estimate is based on assumptions made on dumping and refilling tanks, and on domestic purposes (showers, toilets and refreshments). The annual volume of water used on the CPL was estimated to be 546 kL. This is 42 % of the total annual volume of water used on the whole Brass Division. On the CPL the greatest amount of water (97 %) was used for the flowing rinse tanks. The lowest amount of water was used for refilling the static rinse tank and process tanks.

The two major water users in the Brass Division were water used for the flowing rinses and toilets. The toilets were the biggest water user. However, with the water usage for the toilets there is a lot of uncertainty associated with this value. This is due to workers visiting the toilet more or less than the average of three times a day assumed and this would have a significant impact on the amount of water used.

The water used in the flowing rinse tanks is the second highest value. The rinse water flow rates do show variation, the rates are occasionally very high. The company can use the flowing rinses more efficiently by controlling and monitoring the flow rates, thereby preventing the unnecessary use of water.

The estimated annual water consumption based on the Umgeni Municipality bills, used in the Brass Division was approximately 3499 kL. The expected water usage (see Table 8.14) is only 37 % of the annual billed water consumption. The difference between the actual and estimated water usage is greater than the acceptable error of 20 % as cited by Envirowise.[87] This discrepancy in values could be due to a possible leak in the Brass Division or variations in the flow rates of the flowing rinses. The flow rates are adjusted manually and from the results they are not constant and these flow rates are only measured on the sampling day. Therefore the flow rates could have been set higher on other days and this would increase the water usage on the CPL. Another cause might be underestimation of the toilet usage, the water used for the toilets accounted for the highest volume of water used in the Brass Division. Therefore if the workers visited the toilets more than average it would cause a significant increase in the water usage.

8.4 Drag-out Determinations

The drag-out volumes are significant as they help identify potential waste minimisation opportunities. Some of the techniques used to reduce drag-out were discussed in Section 3.4.3. The methods used to determine drag-out volumes are not simple and there are many difficulties associated with determining these volumes as cited in literature[81]. In this work the drag-out estimations were made using the concentration data (from Tables 7.15, 7.16, 7.19, 7.21 and 7.25) for the elements in Table 8.15. The elements were selected according to their abundance in the particular rinse solution. The operating cycle (OC) is defined as the time period between dumping and refilling the rinse solution tanks and is presented in Appendix C for each rinse stage. Rinse tanks 5, 6, 9 13, 14 and 19 have been excluded from these calculations as their preceding tanks are rinse solutions therefore there is no real drag-in from the process solutions coming into these tanks.

Table 8.15 Rinse tanks and their major element

Rinse tank	Element
2	Na
4	Na
8	S
12	Ni
18	S

The drag-out estimations using the concentration data were based on the following relationships and assumptions:

- The change in concentration of the abundant element (either Na, S and Ni) in the rinse solution (T_n) is due to the drag-out coming into that solution from the previous tank(T_{n-1})
- The Na, S or Ni concentration of T_n was taken as the difference between the Na, S or Ni concentration at the start of the operating cycle and at the end of the cycle

- The mass of Na, S or Ni dragged into solution can be calculated using Equation 8.7

$$\text{Mass of Na in } T_n = \text{Concentration of Na in } T_n \times \text{Solution Volume in } T_n \qquad \textit{Equation 8.7}$$

- The mass of Na, S or Ni accumulating in the rinse solution (T_n) is equal to the mass taken out of the previous solution (T_{n-1})
- The volume of drag-out coming into a solution is related to the concentration of Na, S or Ni in the previous solution according to equation 8.8

$$\text{Drag - out volume into } T_n = \frac{\text{Mass of Na in } T_n}{\text{Concentration of Na in } T_{n-1}} \qquad \textit{Equation 8.8}$$

- The concentration of T_{n-1} is taken as the average concentration of Na, S or Ni during the operating cycle.
- The drag-out rate is the ratio between the drag-out volume and the surface area treated during the operating cycle, and is calculated using Equation 8.9.

$$\text{Drag - out rate (ml/m}^2\text{)} = \frac{\text{Drag - out volume (ml)}}{\text{Surface area treated (m}^2\text{)}} \qquad \textit{Equation 8.9}$$

Table 8.16 Estimation of drag-out volumes using analytical results for Tank 2

Rinse Solution (T_n)	**Previous Solution (T_{n-1})**	**OC**	**Mass of Na in T_n at the OC end (mg)**	**Average concentration of Na in T_{n-1} (mg/L)**	**Drag-out volume (ml)**	**Surface area treated (m^2)**	**Drag-out rate (ml/m^2)**
Tank 2	Tank 1	1	3834	4858	789	19.2	**41**
		2	6873	5415	1269	161	**8**
		3	5210	5299	983	190	**5**
		4	3470	5281	657	25.5	**26**
		5	790	5010	158	56.9	**3**

Table 8.17 Estimation of drag-out volumes using analytical results for Tank 4

Rinse Solution (T_n)	Previous Solution (T_{n-1})	OC	Mass of Na in T_n at the OC end (mg)	Average concentration of Na in T_{n-1} (mg/L)	Drag-out volume (ml)	Surface area treated (m^2)	Drag-out rate (ml/m^2)
Tank 4	Tank 3	1	38.4	982	39	19.2	**2**
		2	755	1000	755	161.3	**5**
		3	647	962	672	190.5	**4**
		4	332	1171	284	42.9	**7**

Table 8.18 Estimation of drag-out volumes using analytical results for Tanks 8

Rinse Solution (T_n)	Previous Solution (T_{n-1})	OC	Mass of S in T_n at the OC end (mg)	Average concentration of S in T_{n-1} (mg/L)	Drag-out volume (ml)	Surface area treated (m^2)	Drag-out rate (ml/m^2)
Tank 8	Tank 7	1	9152	4085	2240	181	**12**
		2	39754	6813	5835	191	**31**
		3	650	8039	81	43	**2**

Table 8.19 Estimation of drag-out volumes using analytical results for Tank 12

Rinse Solution (T_n)	Previous Solution (T_{n-1})	OC	Mass of Ni in T_n at the OC end (mg)	Average concentration of Ni in T_{n-1} (mg/L)	Drag-out volume (ml)	Surface area treated (m^2)	Drag-out rate (ml/m^2)
Tank 12	Tanks 20 & 21	1	493	1110	444	68.1	**7**
		2	501	1474	340	112	**3**
		3	1685	1791	941	190.5	**5**
		4	2702	1743	1550	42.9	**36**

Table 8.20 Estimation of drag-out volumes using analytical results for Tank 18

Rinse Solution (T_n)	Previous Solution (T_{n-1})	OC	Mass of S in T_n at the OC end (mg)	Average concentration of S in T_{n-1} (mg/L)	Drag-out volume (ml)	Surface area treated (m^2)	Drag-out rate (ml/m^2)
Tank 18	Tank 17	1	6004	19090	315	68.1	**5**
		2	360.8	16490	22	76.4	**0.3**
		3	1662	7890	211	231	**1**
		4	461	6880	67	42.9	**2**

Typical average drag-out rates are reported in literature[81,102] for vertical and horizontally hung workpieces. These values are presented in Table 8.21.

Table 8.21 Literature values for good, intermediate and poor drag-out rates for horizontally and vertically hung workpieces

	Drag-out Volume (ml/m^2) [81,102]		
	good	**intermediate**	**poor**
vertically hung	10-40	70-110	150-200
horizontally hung	30-70	-	380

Certain workpieces such as hinges and hasp & staples are hung horizontally on a jig. While other workpieces for example casement handles and flush bolts are wired vertically onto the jig. The drag-out rates for Tanks 2, 4, 8, 12 and 18 (see Tables 8.16 to 8.20) are generally good to excellent. Tanks 4 and 18 consistently showed drag-out rates below the "good drainage range". None of the calculated drag-out rates were significantly outside the "good drainage range". This suggests that the line operators are practicing good drainage methods to minimise the volume of drag-out going into the rinse tanks and there is some level of control exerted over minimising drag-out on the CPL. Indeed, given the low drag-out rates, flush rates in the relevant tanks could even be decreased below current values.

8.5 Estimation of Effluent Stream Concentration

According to the 1998 trade effluent by-laws (see Table 8.22) no individual or industry may discharge substances into the sewerage system with concentrations that exceed limits specified by the Pietermaritzburg-Msunduzi Transitional Local Council. The substances and their specified concentrations are shown in Table 8.22.

Table 8.22 The effluent concentrations limits for substances discharged into the sewer[126]

Substance	Concentration (mg/L)
Solids in suspension	400
Grease and mineral oil, tar and tar oils not dissolve in the aqueous phase	50
Animal and vegetable oils, fats or waxes	250
Total sulfates (SO_4)	250
Sulfides (S)	25
Copper (Cu)	5
Nickel (Ni)	5
Zinc (Zn)	5
Cadmium (Cd)	1
Cobalt (Co)	5
Chromium {Cr(III)}	25
Chromium {Cr(VI)}	0
Hydrocyanic acid and cyanides or other cyanogen compounds (HCN)	10
Molybdenum (Mo)	1
Lead (Pb)	5
Mercury (Hg)	1
Phosphate (P)	20
Arsenic (As)	1
Boron (B)	5
Fluoride (F)	5
Free and Saline Ammonia (N)	80
Selenium (Se)	1
Total Dissolved Solids	5000
Total Sugars and Starch	1000
Total Kjeldahl Nitrogen	100

According to the effluent by-laws, no effluent may be discharged into the sewer that:

- has a pH value less than 6.5 or greater than 9.5.
- has an electrical conductivity greater than 4000 µS/cm

Rinse water solutions exiting the tanks into the effluent stream contain unused raw materials, impurities in the raw materials, by-products and contaminants released from the surfaces of the workpieces. The effluent stream from the CPL goes through a gutter, and is discharged directly into the sewerage system. There was no means of measuring the effluent composition directly so a procedure was developed based on the following assumptions:

- the tanks which are discharging into the effluent stream are the
  - soak cleaner rinse (Tank 2)
  - electrocleaner countercurrent rinse (Tank 4)
  - Galtin countercurrent rinse (Tank 8)
  - nickel countercurrent rinse (Tank 12)
  - neutralizer rinse (Tank 18)
- the flow rate for the effluent stream is the sum of all the individual tank discharge flow rates into the effluent stream. These are represented as flow rates from Tanks 2, 4, 8, 12 and 18 in Equation 8.10 below

Total Effluent Flow Rate (L/min)	=	Flow Rate from Tank 2	+	Flow Rate from Tank 4	+	Flow Rate from Tank 8	+	Flow Rate from Tank 12	+	Flow Rate from Tank 18

Equation 8.10

- An estimation of the concentration of the elements present in the effluent stream is made using the following equations with Na as an example

Mass flow rate of Na (mg/min)	=	Discharge concentration (mg/L)	x	Flow Rate of Rinse Tank (L/min)	*Equation 8.11*

Total Mass Flow Rate of Na in Effluent Stream (mg/min)	=	Mass of Na from Tank 2	+	Mass of Na from Tank 4	+	Mass of Na from Tank 8	+	Mass of Na from Tank 12	+	Mass of Na from Tank 18

Equation 8.12

$$\text{Concentration of Na in the Effluent Stream (mg/L)} = \frac{\text{Total Mass of Na in the Effluent Stream (mg/min)}}{\text{Total Effluent Flow Rate (L/min)}}$$

Equation 8.13

Table 8.23 Estimated total concentration of major elements in the effluent stream

Date	Total Concentration in Effluent Stream (mg/L)									
	Na	**P**	**SO_4^{2-}**	**Si**	**Ni**	**Cr**	**Cu**	**Zn**	**B**	**Pb**
13/02	15.3	10.1	28.2	2.9	1.9	0.17	0.07	0.21	0.17	0.17
20/02	5.8	3.2	16.7	1.1	2.2	0.31	0.02	0.06	0.26	0.02
27/02	2.6	1.6	16.3	0.54	1.1	0.09	0.01	0.04	0.11	0.01
6/03	6.6	3.3	66.7	0.97	3.2	1.09	0.01	0.06	0.28	0.01
13/03	4.0	1.5	25.7	0.73	1.6	0.15	0.01	0.06	0.14	0.01
20/03	20.7	14.8	38.3	3.5	2.5	0.19	0.06	0.19	0.21	0.15
27/03	21.8	15.9	11.9	4.0	2.4	0.13	0.06	0.22	0.21	0.28
03/04	17.3	8.2	7.3	3.2	0.15	0.09	0.03	0.05	0.06	0.13
11/04	30.2	1.3	4.9	0.81	0.17	0.01	0.02	0.01	0.04	0.01
17/04	37.0	**23.1**	14.7	6.2	1.3	0.22	0.08	0.31	0.17	0.43
24/04	36.0	**22.4**	18.5	5.6	**7.2**	0.24	0.30	1.04	0.58	0.42
09/05	8.6	2.8	5.3	1.6	0.13	0.07	0.03	0.11	0.07	0.07
15/05	29.3	17.2	14.5	5.1	4.8	0.16	0.03	0.07	0.39	0.15
22/05	17.5	7.8	14.8	3.3	4.3	0.15	0.01	0.04	0.35	0.07
29/05	21.4	9.5	7.1	3.9	0.54	0.15	0.02	0.05	0.19	0.10
5/06	14.1	8.0	8.4	2.7	1.7	0.12	0.03	0.04	0.25	0.09
12/06	13.7	5.9	7.6	2.6	1.2	0.09	0.01	0.05	0.16	0.05
19/06	20.2	12.1	17.8	3.5	**5.5**	0.15	0.02	0.05	0.44	0.11

The estimated concentrations of most elements in the effluent stream (see Table 8.23) are within the specified limits shown in Table 8.22. The P concentration in the effluent exceeds the limit of 20 mg/L on the 17/04 and 24/04. On the 24/04 and the 19/06 the Ni concentration exceeded the limit of 5 mg/L.

According to the limits specified by the Pietermaritzburg-Msunduzi Transitional Local Council the pH of the effluent should not be less than 6.5 or greater than 9.5. The average pH values for the rinse solutions in tanks 2, 4 and 8 are 11.8, 10.3 and 3.71 respectively (see Tables 7.33, 7.34 and 7.37). The pH in tanks 2 and 4 therefore exceeds the maximum allowable limit of 9.5 and tank 8 has a much lower pH than the specified limit of 6.5. The pH of these tanks are important as their rinse water is discharged directly to the

effluent stream and into the sewerage system. Unlike the estimations of elemental concentrations the pH in the mixed effluent stream cannot be easily calculated from the pH of the individual streams, because of possible reactions that might occur. Since the effluent stream is a mixture of the individual rinse solutions which have a range of pH values, the mixture of rinse water may possibly react and neutralize the pH of the effluent stream, however this is uncertain. The company therefore needs to analyse the effluent stream to make sure the pH is within the acceptable range.

8.6 True Cost of Waste Analysis

The waste from the rinse solutions entering the effluent stream contains unconverted chemicals from the process solutions. The true cost of waste value takes into account the cost of these unused chemicals.

The chromium concentration in the effluent stream was used to determine the raw material chemical wastage. The source of chromium is Lumina 34 (CrO_3), the chemical used in the chromium plating tank (Tank 15). The estimated concentration of the element chromium in the effluent was calculated in Section 8.5. There were no chemicals purchased during the monitoring period. Therefore the price for the chemicals already in stock and currently being used on the CPL was used to calculate the true cost of waste.

The waste stream cannot be monitored or analysed as mentioned previously (Section 8.5) as it leaves the CPL through a gutter that collects the waste and was not accessible for sampling. The mass of chromium (mg/min) in the effluent stream was calculated in Section 8.5 using the rinse flow rate and the discharge concentration (see Equations 8.11 and 8.12). The mass of Lumina 34 was calculated using Equation 8.14, in this equation the time refers to the total number of minutes for the sample period (see third column in Table 8.23). The cost of Lumina 34 is R52/kg (R0.052/g). This cost and the mass of Lumina 34 were used to cost the wasted raw material (using Equation 8.15). These values are presented in Table 8.24.

$$\text{Mass of Lumina 34 } (CrO_3) \text{ in effluent (g)} = \frac{100}{52} \times \text{Mass of Cr (g / min)} \times \text{time (min)}$$

Equation 8.14

$$\text{Cost (Rands)} = \text{Cost of Lumina 34 (Rands/g)} \times \text{Mass of Lumina 34 in effluent (g)}$$

Equation 8.15

Table 8.24 Estimation of the cost of Lumina 34 lost in the effluent stream

Sample Period	Mass of Cr (g/min)	Time (min)	Mass of Lumina 34 (g)	Cost of Lumina 34 in Waste (Rands)
1	1.81×10^{-4}	2250	0.78	0.041
2	2.20×10^{-3}	2250	9.51	0.495
3	7.13×10^{-4}	2250	3.09	0.161
4	5.68×10^{-3}	2250	24.56	1.279
5	1.06×10^{-3}	2250	4.57	0.238
6	5.96×10^{-4}	2250	2.58	0.134
7	4.13×10^{-4}	1800	1.43	0.074
8	2.67×10^{-4}	2250	1.15	0.060
9	3.43×10^{-5}	1350	0.09	0.005
10	8.10×10^{-4}	2250	3.50	0.182
11	5.45×10^{-4}	2250	2.36	0.123
12	5.32×10^{-4}	4050	4.14	0.216
13	9.63×10^{-4}	1800	3.33	0.174
14	4.48×10^{-4}	2250	1.94	0.101
15	1.01×10^{-3}	2250	4.39	0.228
16	5.60×10^{-4}	2250	2.42	0.126
17	4.60×10^{-4}	2250	1.99	0.104
	Total cost for 85 days			**3.74**
	Total cost for 238 days			**10.47**

The total annual true cost of waste was estimated to be R10.47. This indicates that there is no significant raw material wastage in the effluent stream and the CPL is therefore being run efficiently with regards to their chemical usage.

8.7 Monitoring and Targeting

Monitoring and targeting involves monitoring the consumption of raw materials and utilities (such as water and energy) as a function of a process variable. Monitoring and targeting is useful in determining waste minimisation opportunities where there is a variable target such as water consumption. It is also helpful in assessing the performance levels of the company, setting obtainable targets or goals for the consumption of a particular resource and the ongoing monitoring and feedback of progress made.

The monitoring and targeting graph in Figure 8.4 shows the water consumption on the CPL as a function of the surface area treated. The Umgeni Municipality water bill for the Brass Division includes the water used both on the CPL and other domestic uses (gardening, showers etc). Therefore the rates used in Section 8.5.5 to determine the water usage by non-CPL activities were estimated and subtracted from the total water usage on the bill to get an approximate value for the water consumption on the CPL. These values are presented in Table 8.25 together with the surface area treated during that time. Also the water meter readings were taken once a month and occasionally once every two months. Therefore it is not possible to estimate the amount of water used on the CPL during the specific sample periods. The amount of water used on the CPL was calculated based on the water bills and the points were plotted against the total surface area treated during that time.

Table 8.25 Water used and total surface area treated during the specified sample periods

Sample period	Water used (kL)	Surface area treated (m^2)
1, 2	413	43.6
3,4,5,6,7	291	170.3
8, 9,10	573	157
11,12	540	25.5
13,14,15,16	454	70

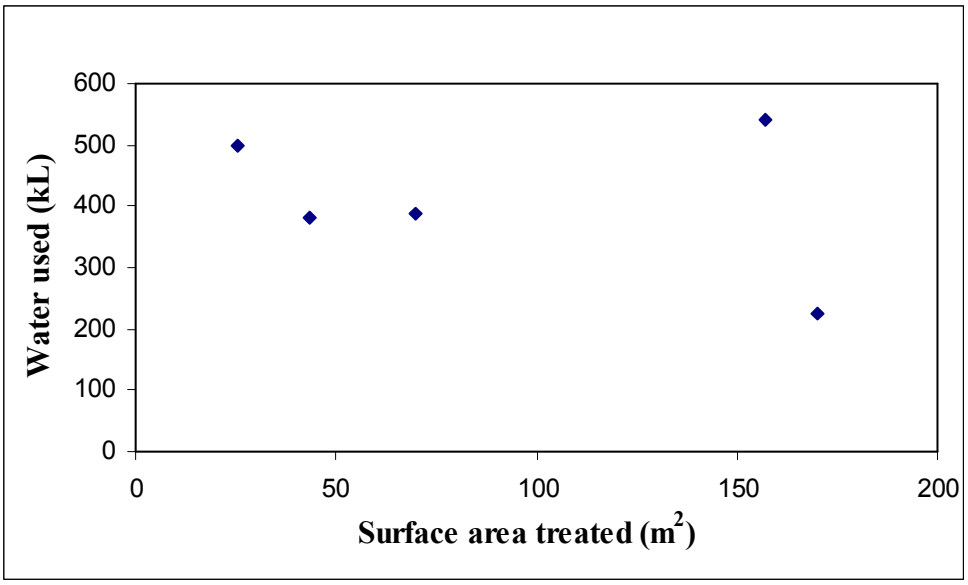

Figure 8.4 XY scatter plot of water consumption as a function of the surface area treated

The graph shows a poor correlation between water consumption and surface area treated. The smallest surface area treated consumed the second largest amount of water and the largest area treated used the least amount of water. This shows that the water is not being utilized efficiently on the CPL. There needs to be more control exerted over the water usage on the CPL. The company should consider investing in a water meter for the CPL to monitor the water usage. A target line could not be drawn as there is no indication of a relationship between the water usage and the surface area treated.

In Section 3.3.4.1 the use of a water economy diagram was discussed. Envirowise published the water economy diagrams which are an example of monitoring and targeting graphs. The water economy diagram (see Figure 3.9) allows a company to compare its performance with other companies in the industry. It gives an indication of how efficiently the company is using water. The water economy graph shows the water usage as a function of the surface area treated.

The water economy diagram requires a knowledge of the total annual surface area treated (m^2/year) and the water usage (m^3/year). The total surface area treated on the CPL during the full monitoring period was 479 m^2, this was converted to an annual figure of 1342 m^2. The water usage for non-CPL activities were estimated and subtracted from the total annual water usage estimated using the Umgeni Municipality bills. This gave an amount of 2700 m^3.

The water economy diagram was drawn (see Figure 8.5) using an appropriate scale in order to plot the points. The target lines are all the same as the water economy diagrams in Figure 3.9. The points were plotted and fell in the worst 25% category. Assuming that this small CPL can be treated in the same way as the survey, this further highlights the fact that water usage on the CPL is not efficient, and requires immediate improvement. The graph also illustrates that the CPL is a much smaller line compared to the other companies used in the survey as the scale used in Figure 8.5 is much smaller than the scale on the water economy diagrams in Figure 3.9.

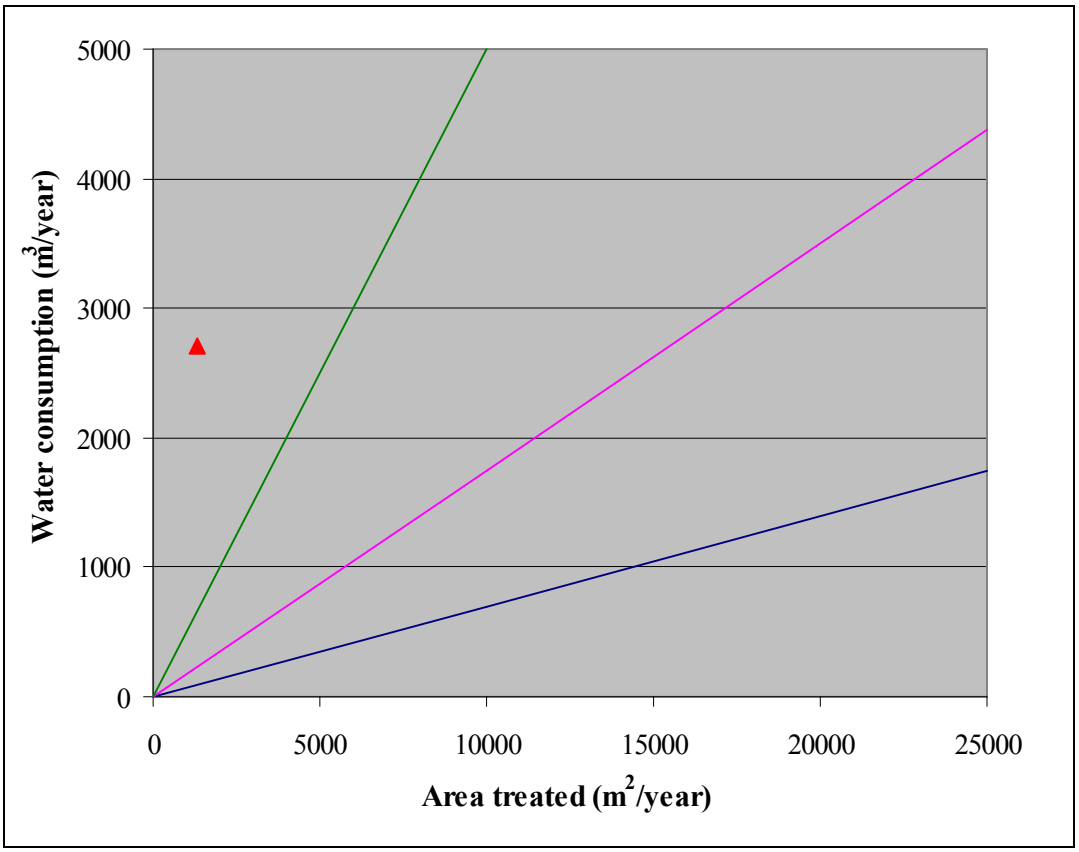

Figure 8.5 Water economy diagram using a smaller scale showing the performance of the CPL

From the XY scatter plot (see Figure 8.4) and the performance of the CPL using the water economy diagrams (see Figure 8.5), the water usage clearly represents a waste minimisation opportunity for the company.

CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

The waste minimisation analysis results show that the water consumption on the CPL presents an important waste minimisation opportunity for the company.

- From the monitoring and targeting results there is no apparent relationship between the water usage and surface area treated on the CPL. Ideally the water usage and surface area should show a good correlation (the largest surface area treated should use the highest volume of water).
- The water economy diagrams illustrate that water usage on the CPL fell into the worst 25% performance category.

This indicates that there is no proper control exerted over water usage on the CPL, and this is possibly leading to the wastage of high volumes of water. The company needs to start monitoring and improving the water usage on the CPL.

There is, however, a large caveat regarding the data used. From the water balance analysis the water usage according to the Umgeni Municipality bills was about three times the estimated water usage. The estimated water usage was based on a number of assumptions which were necessary due to the lack of accurate information. For example the flowing rinses are the biggest water user on the CPL; the flow rates were taken on the sampling day, and were assumed to be the same throughout the sample period. However, this is unlikely as the flow rates were shown to fluctuate during the sampling visits and there was no control exerted over maintaining a constant flow rate.

The true cost of waste analysis shows that there was no significant chemical wastage based on the chromium content in the effluent stream. The projected annual true cost of waste was negligible.

The drag-out rates estimated from chemical analysis were comparable to the values for good drainage cited in literature. This indicates that there is some control exerted over drag-out on the CPL.

The average pH levels in rinse tanks 2, 4 and 8 which discharge directly into the effluent stream were individually not within the acceptable range specified by the Pietermaritzburg-Msunduzi Transitional Local Council. However the pH of the mixed effluent which actually reaches the wastewater system is unknown. The concentrations of the elements analysed fell within the maximum limits.

Again the lack of data and difficulty in obtaining useful data has made certain waste minimisation techniques difficult to perform. The information regarding the date and quantities of chemical additions made into the process tanks and dumping of the rinse tanks is vital in a waste minimisation audit. However these data could not be gathered easily as the company keeps no records of this information. As a result the scoping audit could not be carried out as there was no proper stock control regarding the quantity of chemicals used and still in stock for the CPL. The lack of available data is not uncommon and has been cited in literature as a problem when conducting a waste minimisation audit.[127,128] The characterisation of the process and rinse solutions shows that there is a lot of uncertainty with additions made into the process tanks and dumping of the rinse tanks. Certain additions are made into the process solutions that are not recorded on the Analysis Reports or by the line operators. The rinse tank profiles indicate that the rinse tanks are sometimes dumped too frequently, which leads to the wastage of water.

Conductivity analysis can provide an effective method for estimating the build up of dissolved salts in the rinse tanks and could be a beneficial method for the company to use to determine when the tanks require dumping.

9.2 Waste Minimisation on the Chromium Plating Line

There are a number of waste minimisation measures that are already being undertaken on the CPL. These include:

- Countercurrent rinsing is used for 3 of the rinse stages in order to maintain a low rinse water flow in the running rinses.
- There are drag-out tanks which follow the nickel and chromium plating tanks.
- The nickel plating solutions undergo continuous filtration.
- The nickel anodes are enclosed in fabric bags.
- Fumetrol 140, a fume suppressant is used in the chromium plating tank to form a foam blanket over the solution preventing acid mist emission.
- There is a drain board between the chromium plating bath and the drag-out tank, to capture and channel the run-off solution back into the plating bath as the workpieces are moved between these tanks.

Further possible waste minimisation opportunities that were observed for the CPL include:

- There is no water meter for the CPL.
- There are no records kept of when dumping of the rinse tanks takes place.
- There are no records kept by the line operators of any chemical additions made to the process tanks, for example sodium metabisulfite in the neutralizer tank (Tank 17).
- There are no records of the stock used and still remaining in the store room.
- There is no control exerted over the flowing rinse rates.

9.3 Recommendations

From the waste minimisation audit the following recommendations have been proposed to improve the efficiency of the process:

- the company needs to keep accurate records of chemical additions made into the process tanks, amount of chemicals used and the quantity of chemicals remaining in stores.
- they also need to keep a precise record of when dumping and recharging of the rinse tanks occurs, to ensure that the tanks are not being dumped unnecessarily.
- conductivity measurements can be used as a method to determine when dumping of the rinse tanks should occur.
- the company should invest in a water meter for the CPL, to monitor and keep track of the water used on the CPL.
- they also need to consider replacing the municipality water meters, and read these daily to account for the water usage in the different divisions.
- the unnecessary use of water should be avoided, the mains water supply to the CPL should be turned off during lunch time and tea time.
- a constant flow rate of water to the flowing rinse tanks can be maintained by installing flow restrictors. Thereby controlling the amount of water used.
- an effluent balancing tank should be installed, to prevent pH spikes thereby ensuring the pH of the effluent stream is within the specified limits required for disposal into the sewerage system.
- the company needs to monitor and analyse the effluent stream for pH, conductivity and elemental concentration.

9.4 Lessons Learnt

Conducting this waste minimisation audit has given me the opportunity to gain valuable knowledge and experience both on-site at the factory and in the laboratory. The new skills I have acquired and the experience gained include:

- going on-site to collect samples and conduct measurements.
- identifying the relevant data (both historical and new) required from a company to perform a waste minimisation audit.
- knowledge of how to interpret the data and use it to perform a mass balance, true cost of waste and monitoring and targeting analysis.
- recognizing potential waste minimisation opportunities for a company.

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APPENDIX A

The concentration profile of the process solutions for Tanks 1, 7, 10, 11, 15 and 17 are shown below.

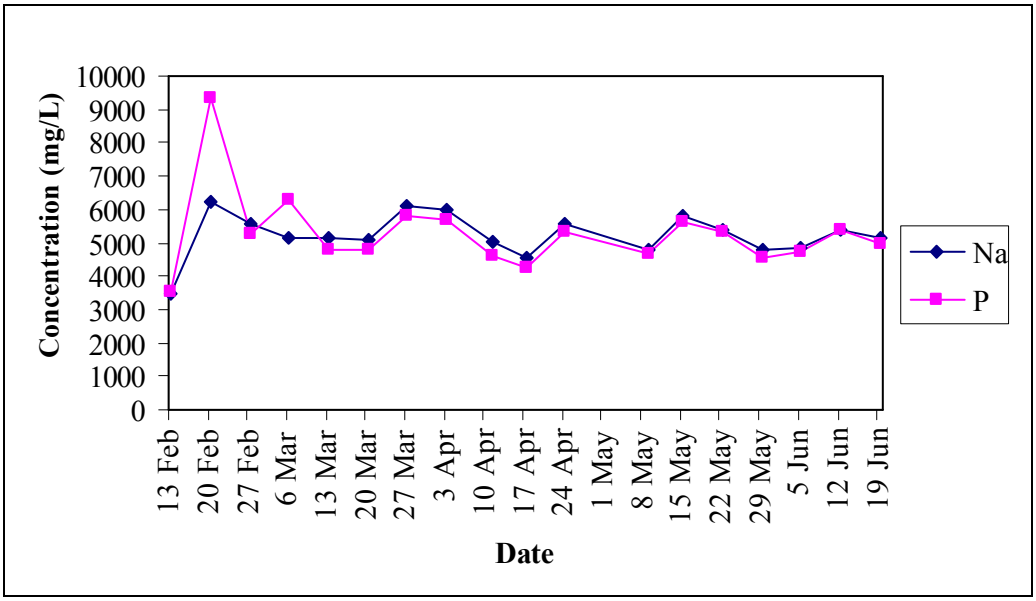

Figure A1 Concentration profile of Tank 1

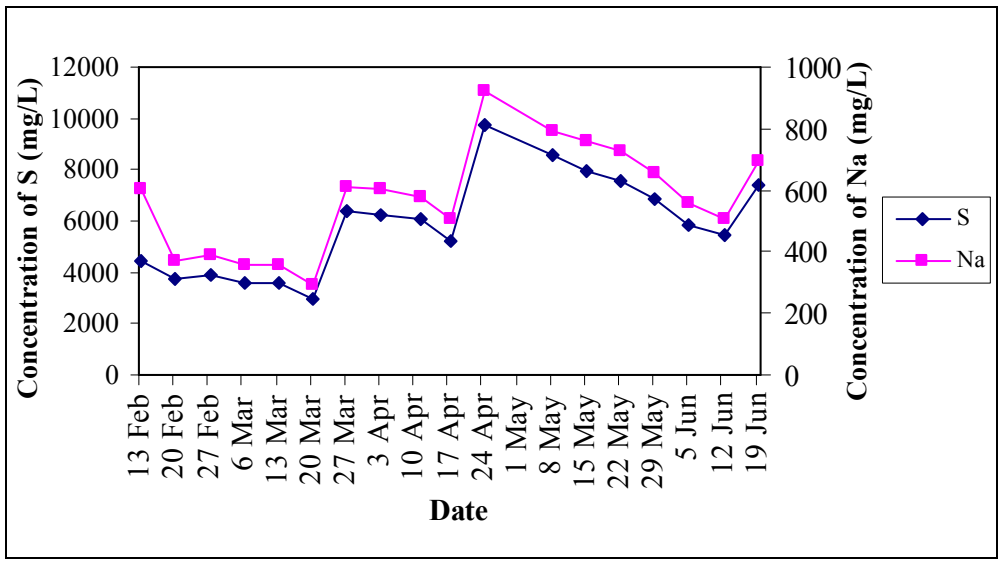

Figure A2 Concentration profile of Tank 7

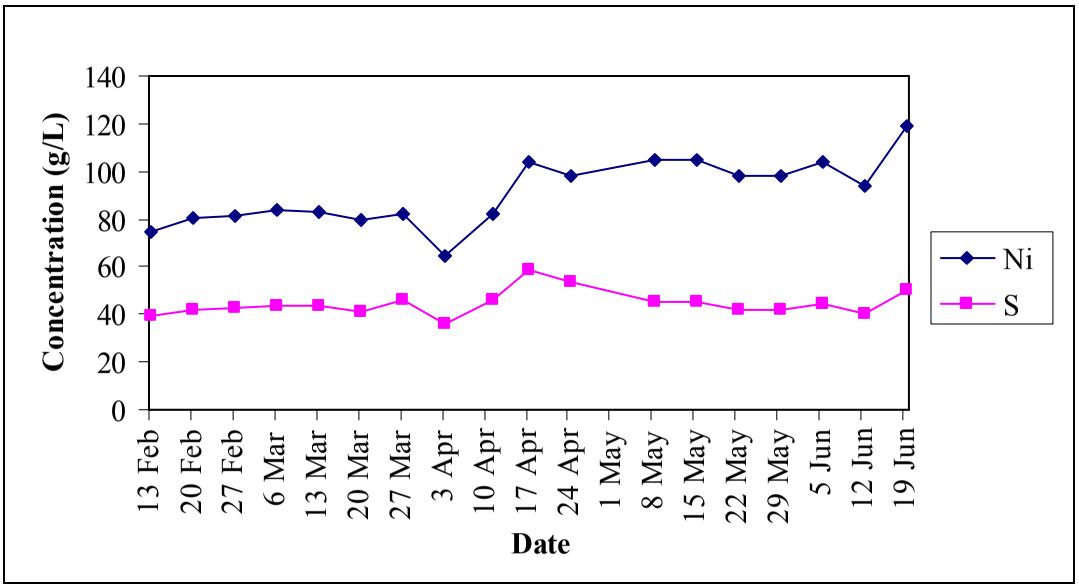

Figure A3 Concentration profile of Tank 10

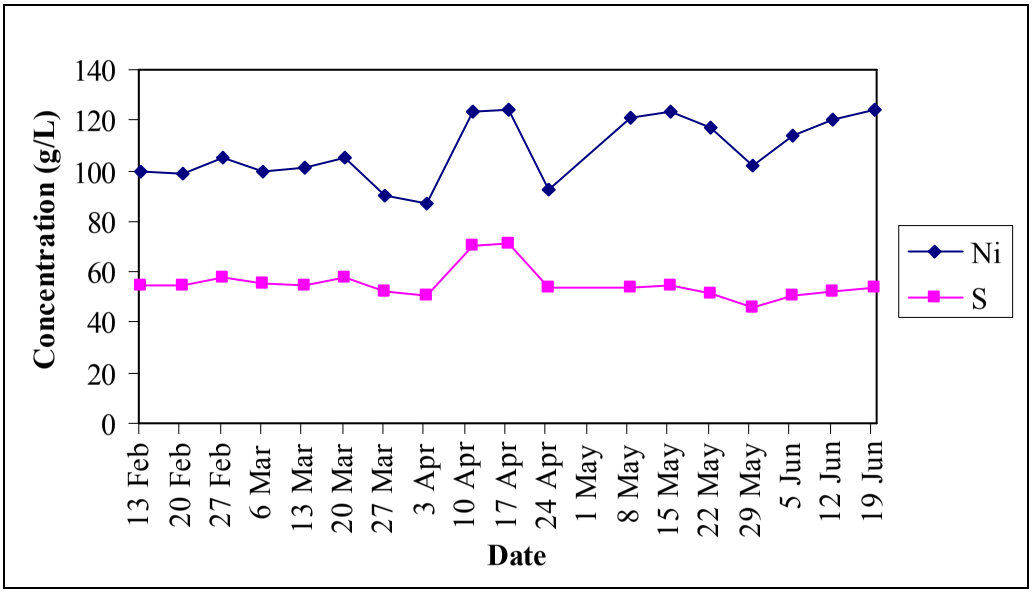

Figure A4 Concentration profile of Tank 11

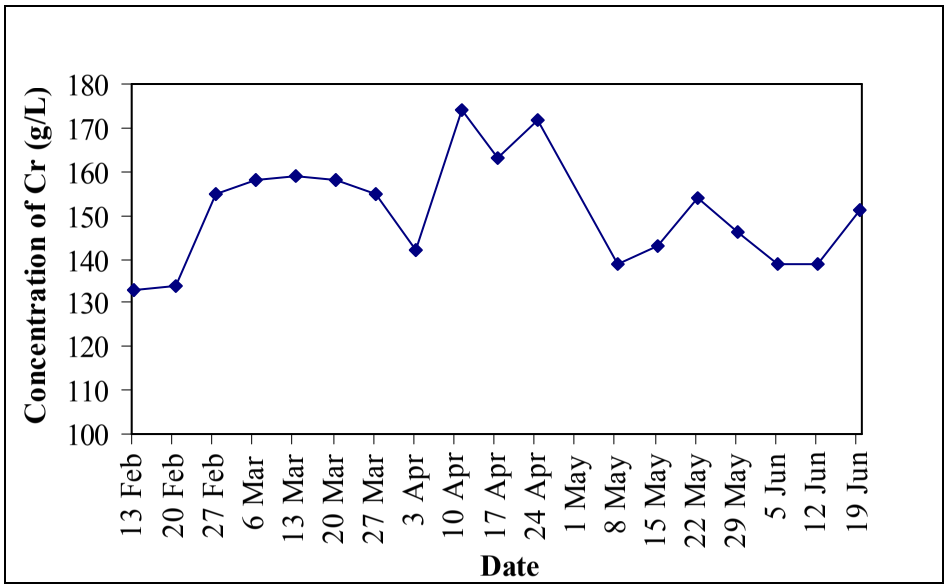

Figure A5 Cr concentration profile of Tank 15

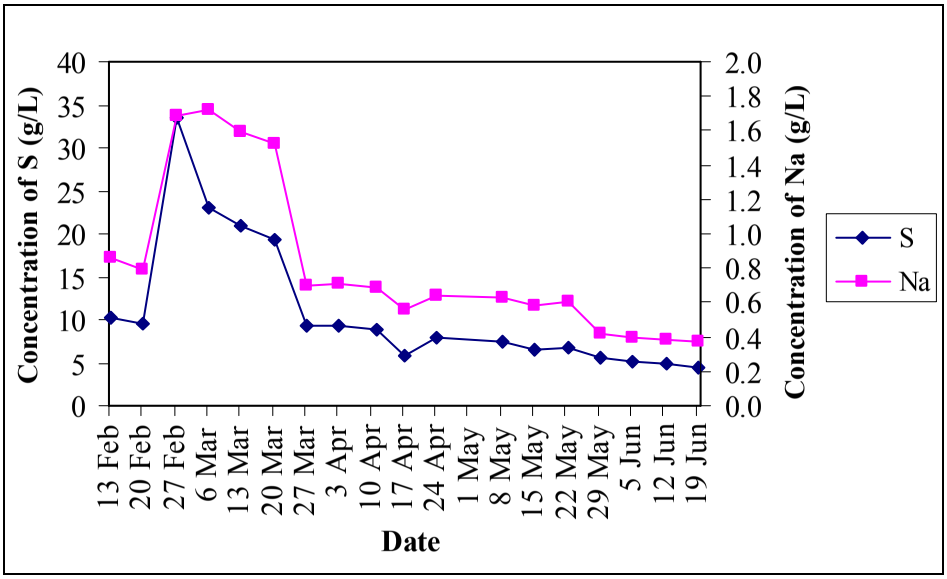

Figure A6 Concentration profile of Tank 17

APPENDIX B

The concentration and conductivity and TDS profiles of the rinse solutions for rinse Tanks 4, 5 , 6, 8, 9, 12, 13, 14, 16, 18, 19 , 20 and 21 are shown below.

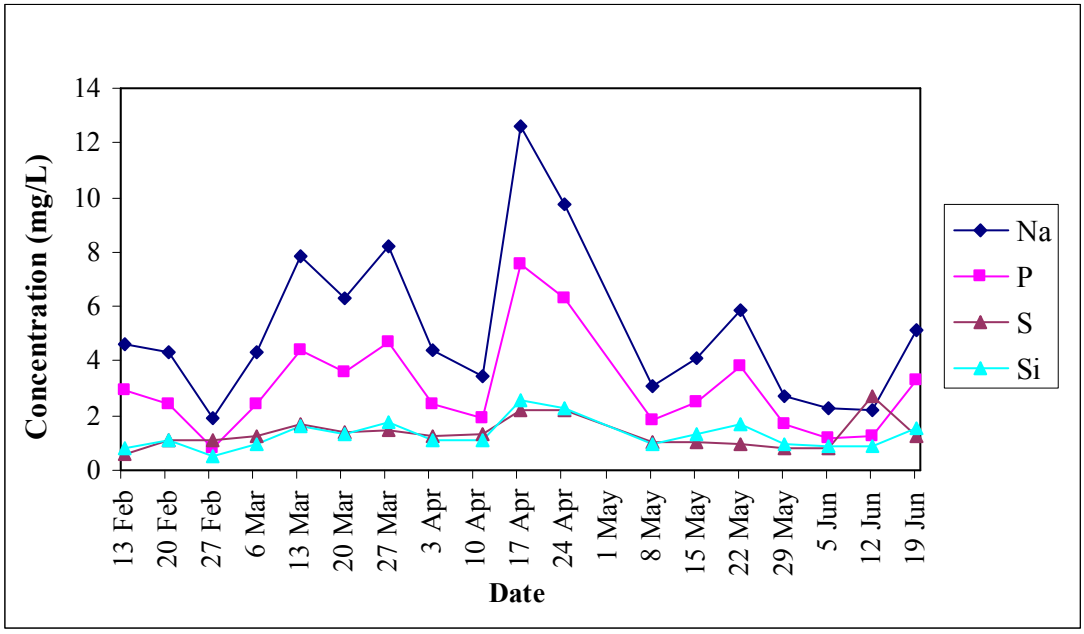

Figure B1 Concentration profile of Tank 4

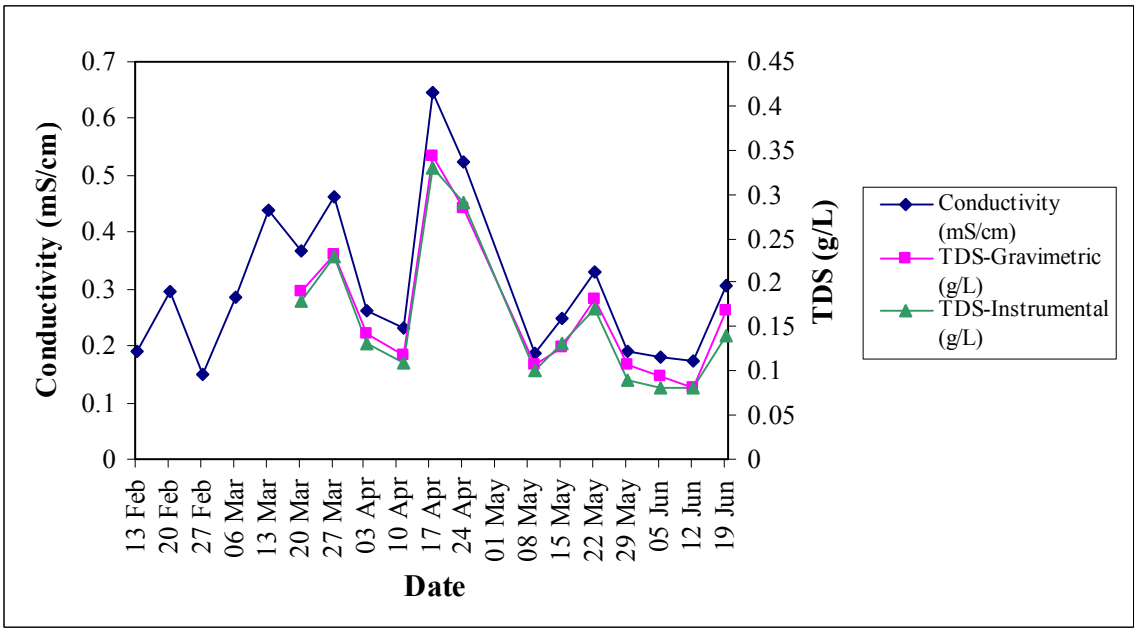

Figure B2 Conductivity and TDS profile for Tank 4

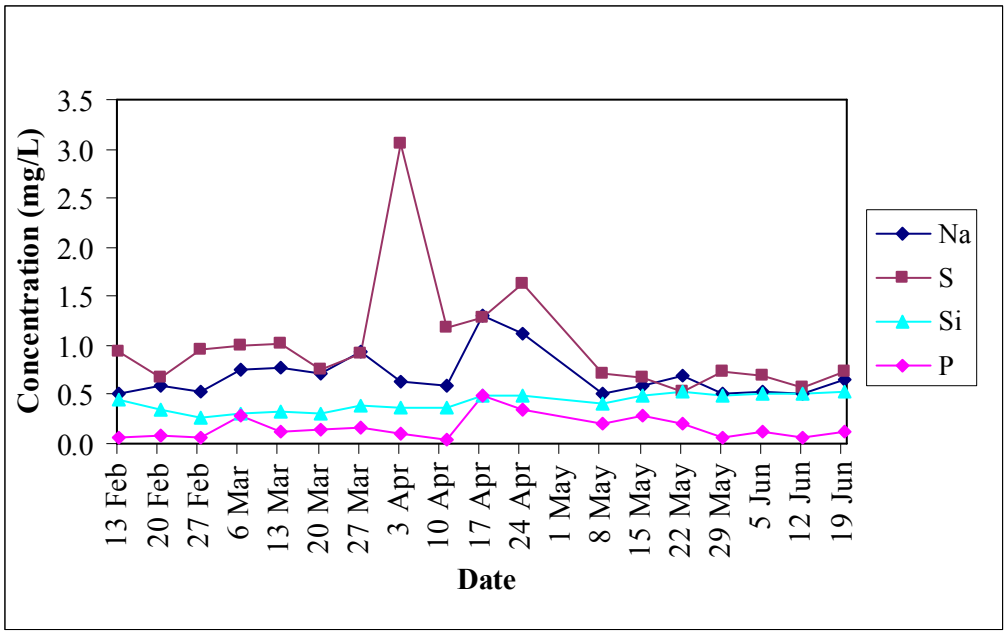

Figure B3 Concentration profile of Tank 5

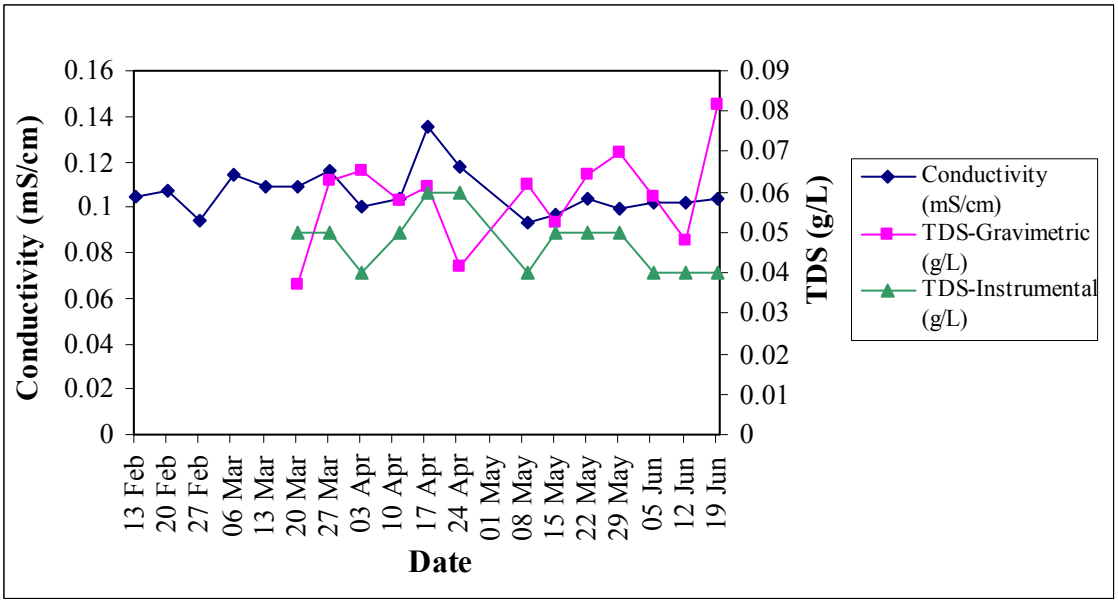

Figure B4 Conductivity and TDS profile for Tank 5

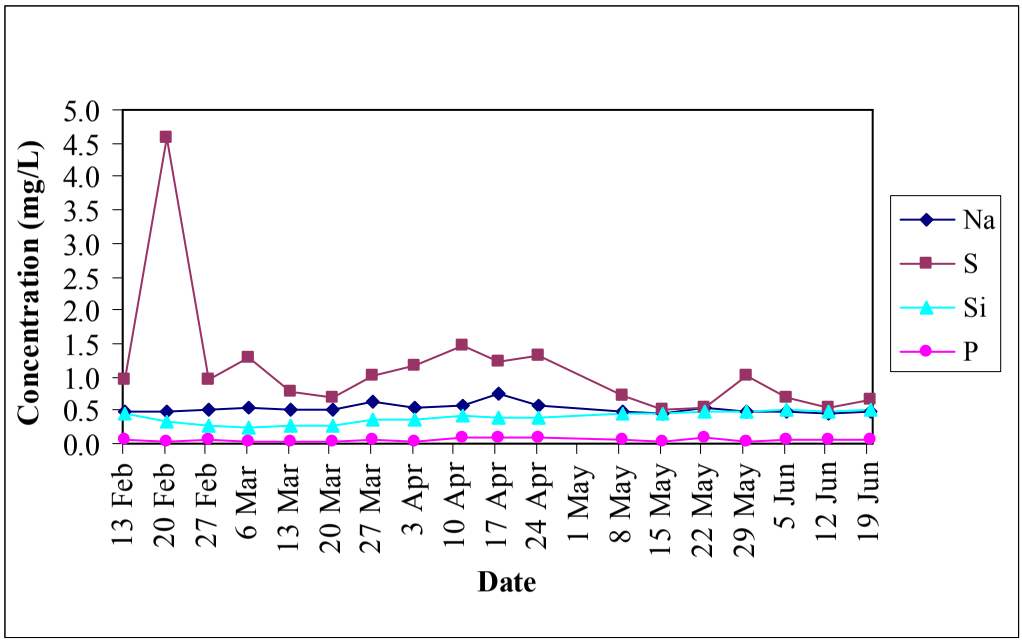

Figure B5 Concentration profile of Tank 6

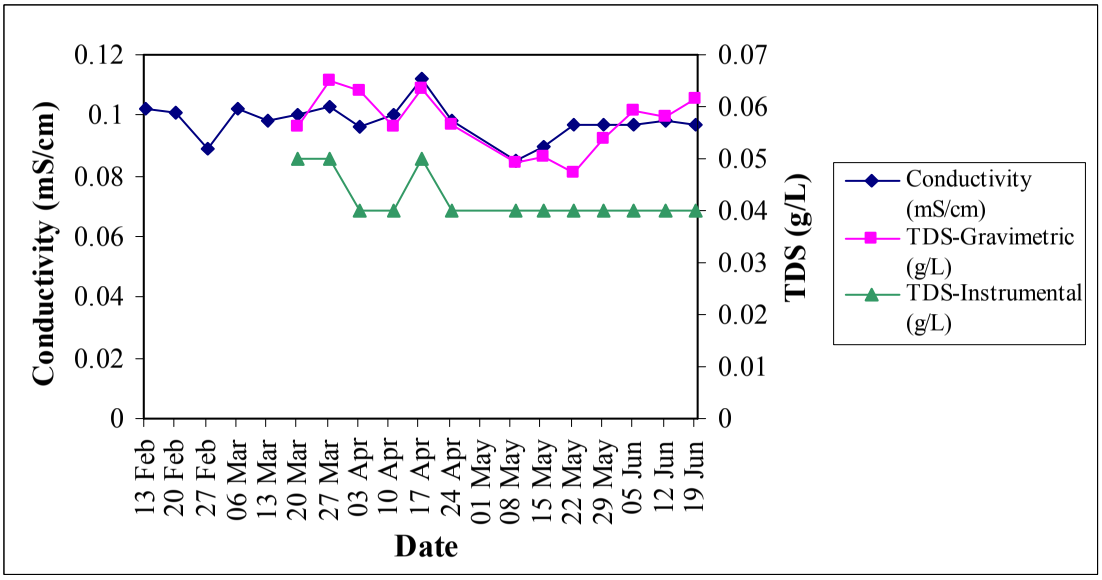

Figure B6 Conductivity and TDS profile for Tank 6

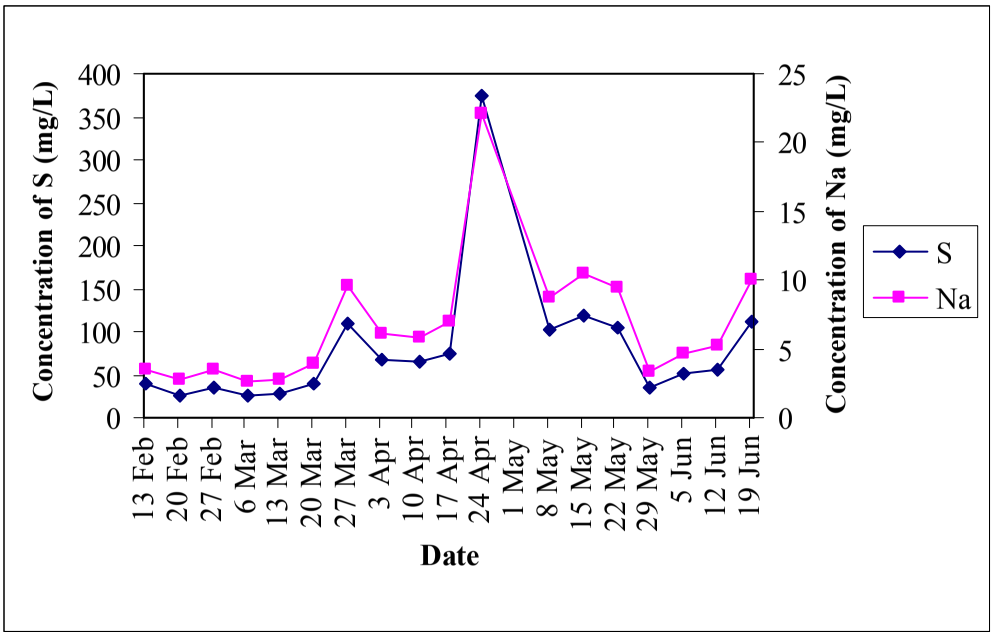

Figure B7 Concentration profile of Tank 8

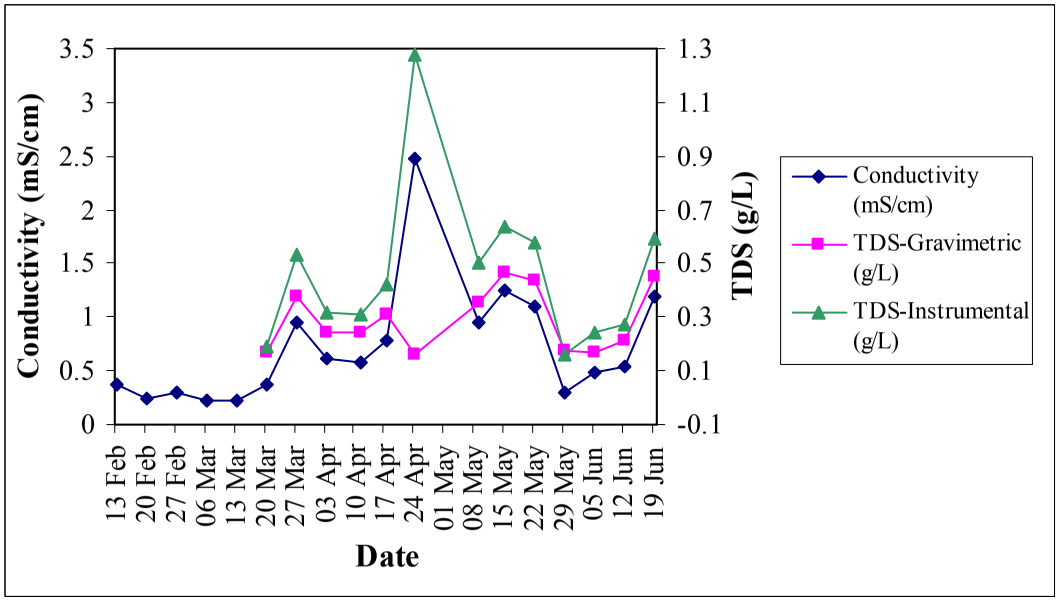

Figure B8 Conductivity and TDS profile for Tank 8

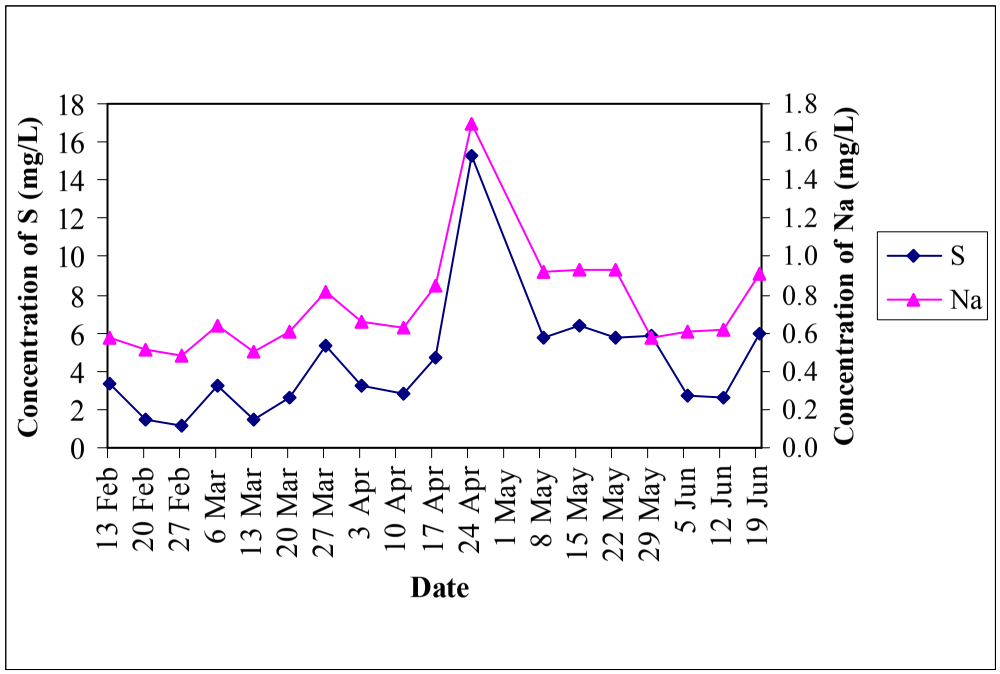

Figure B9 Concentration profile of Tank 9

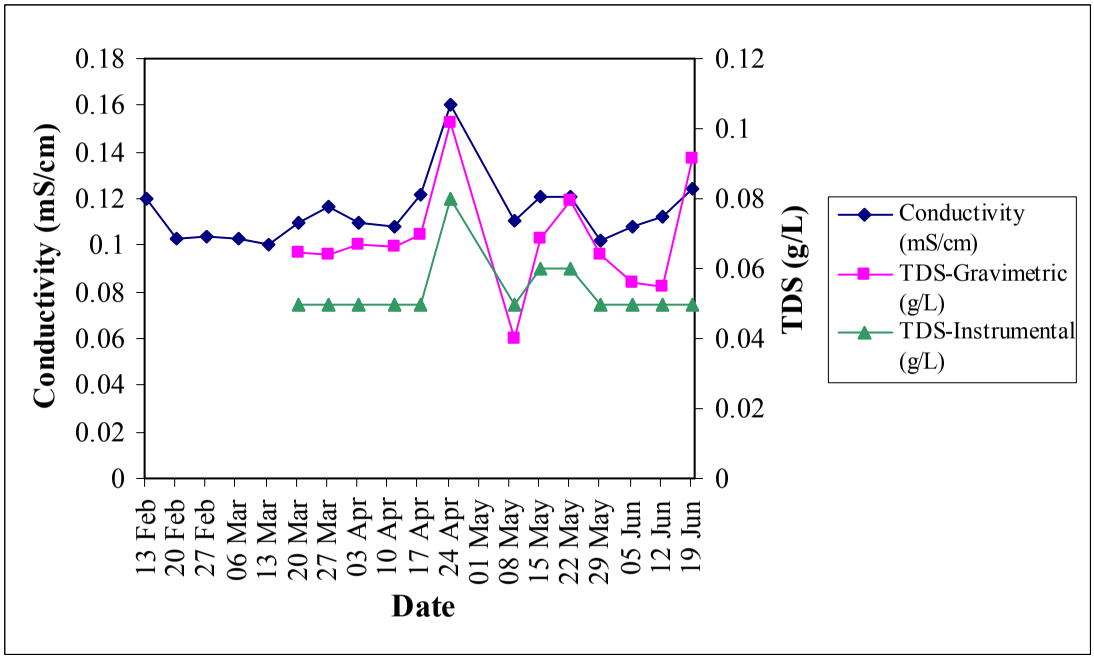

Figure B10 Conductivity and TDS profile for Tank 9

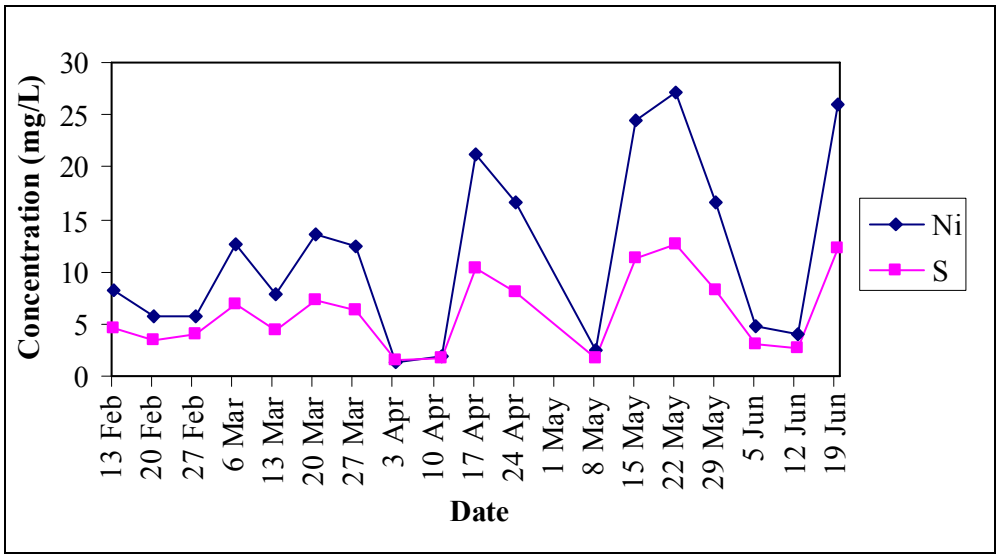

Figure B11 Concentration profile of Tank 12

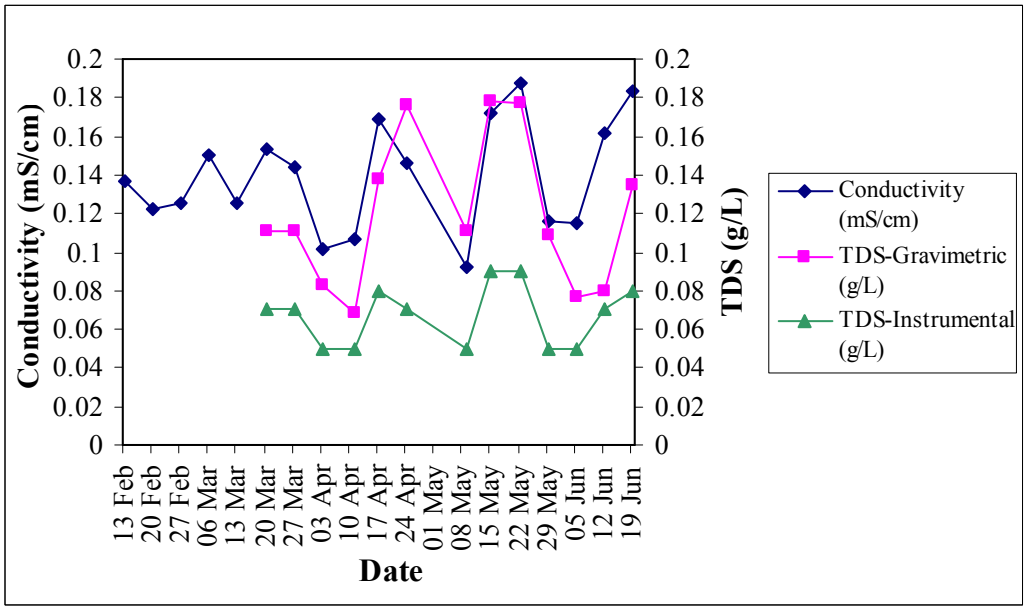

Figure B12 Conductivity and TDS profile for Tank 12

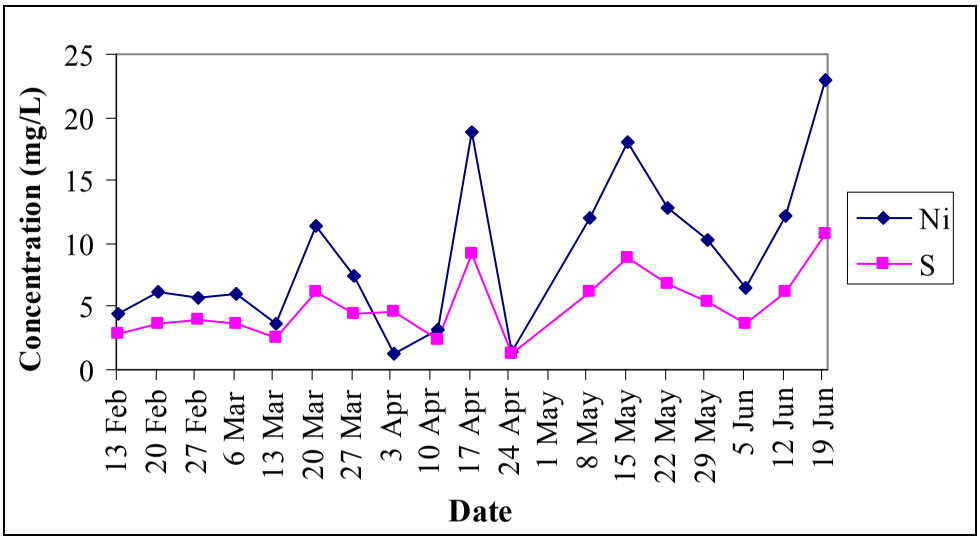

Figure B13 Concentration profile of Tank 13

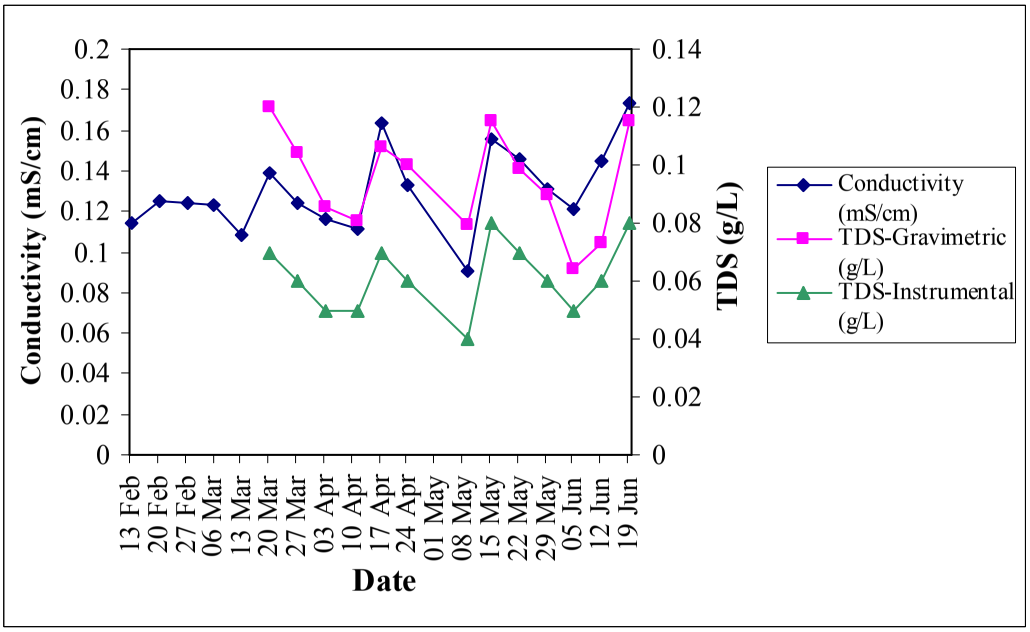

Figure B14 Conductivity and TDS profile for Tank 13

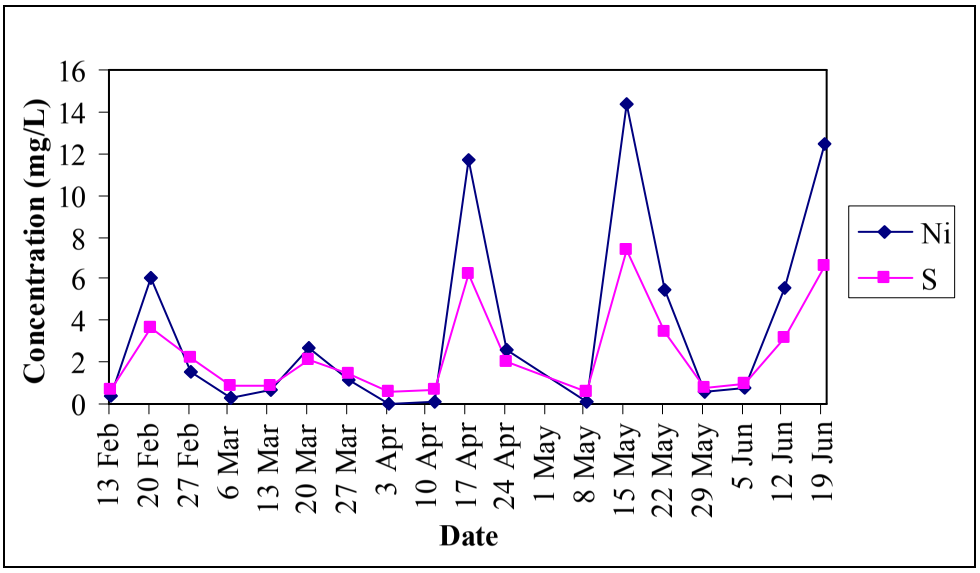

Figure B15 Concentration profile of Tank 14

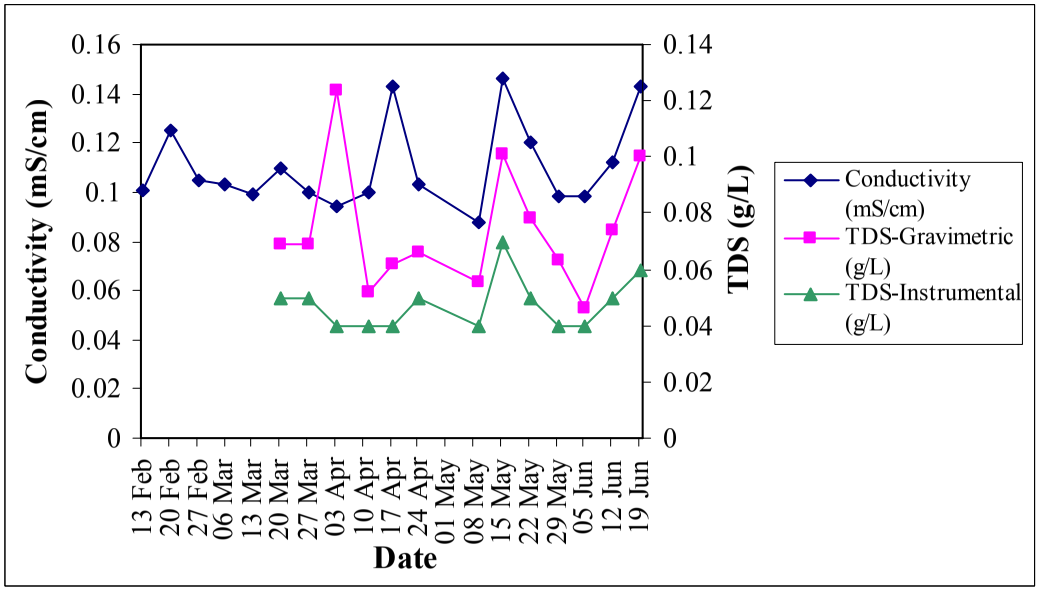

Figure B16 Conductivity and TDS profile for Tank 14

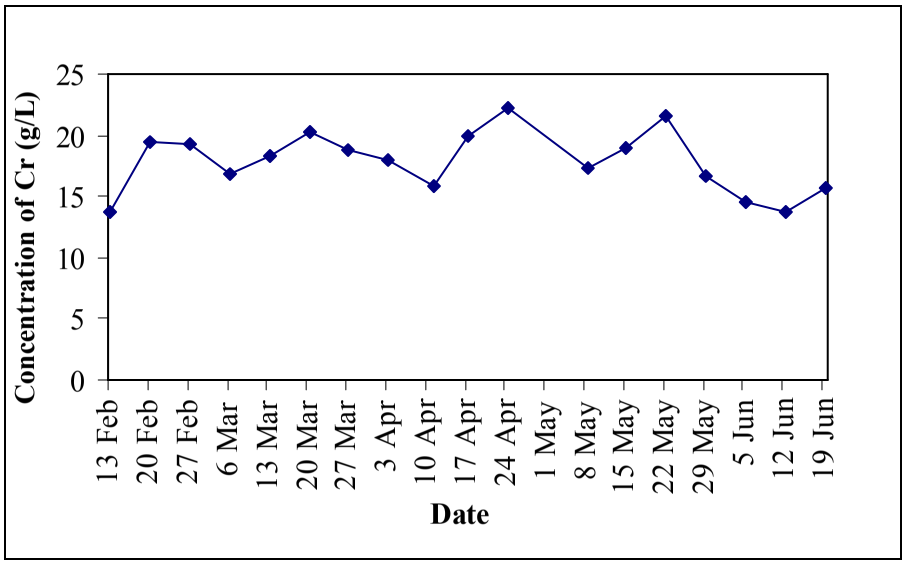

Figure B17 Concentration profile of Tank 16

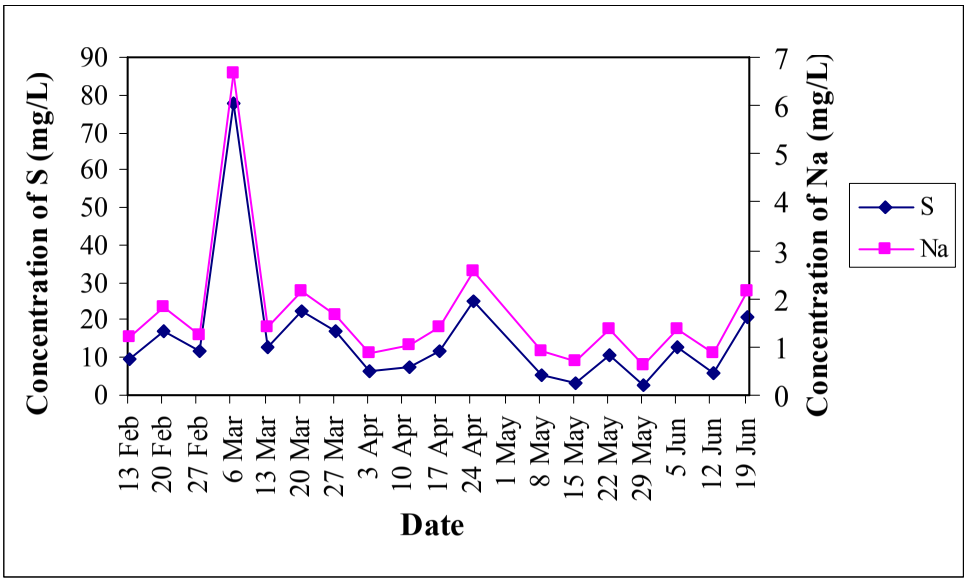

Figure B18 Concentration profile of Tank 18

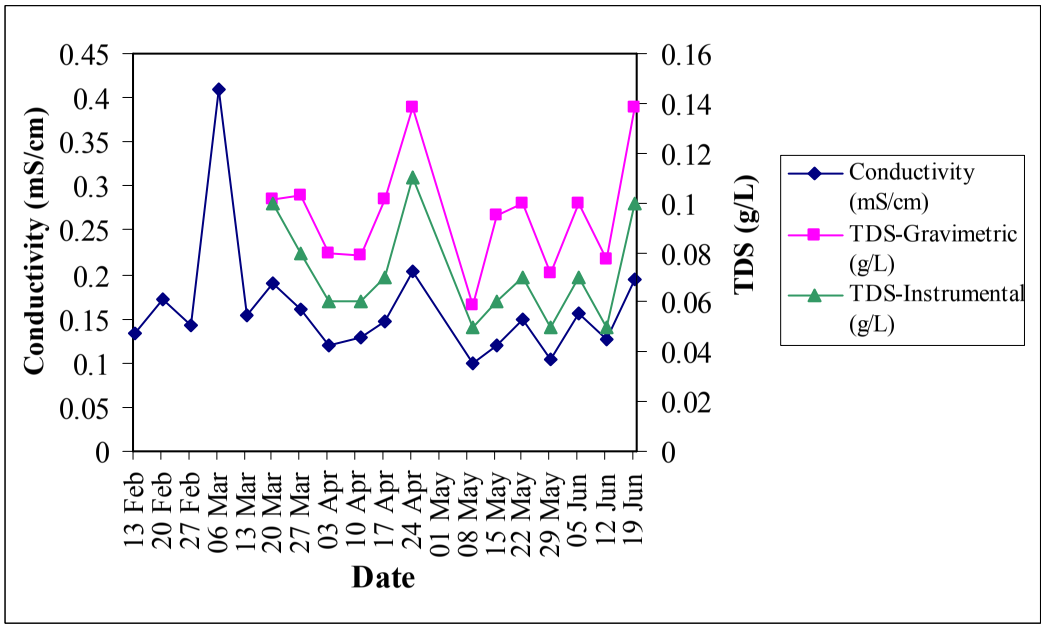

Figure B19 Conductivity and TDS profile for Tank 18

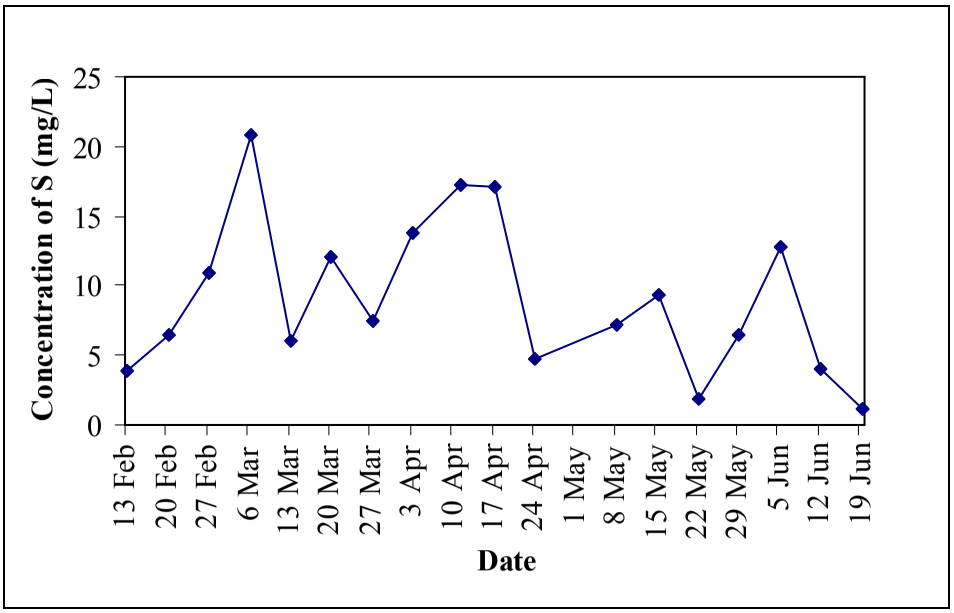

Figure B20 S concentration profile of Tank 19

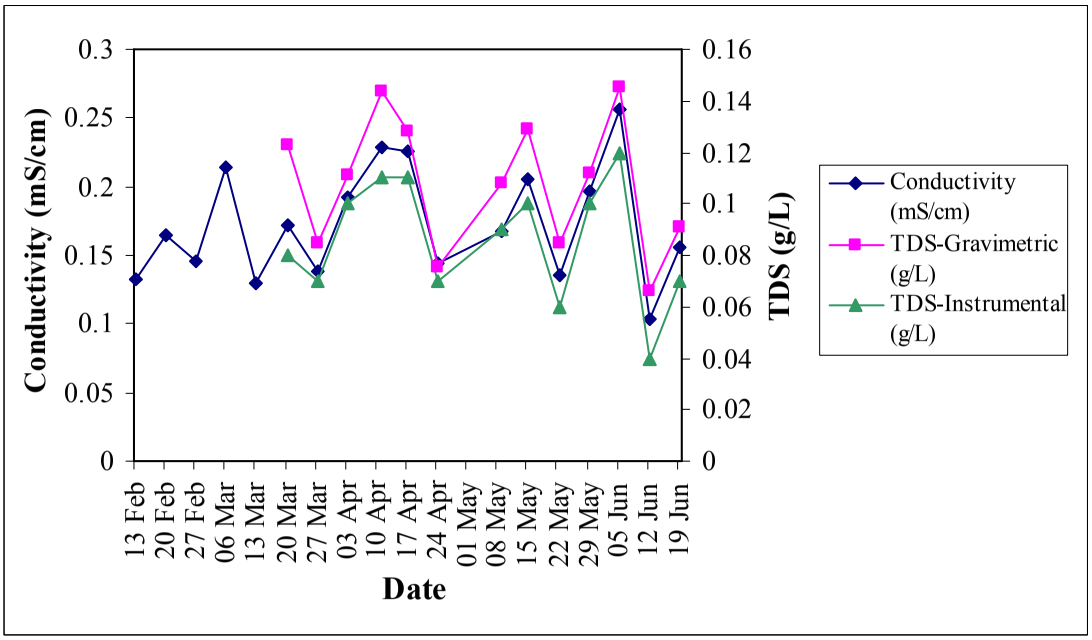

Figure B21 Conductivity and TDS profile for Tank 19

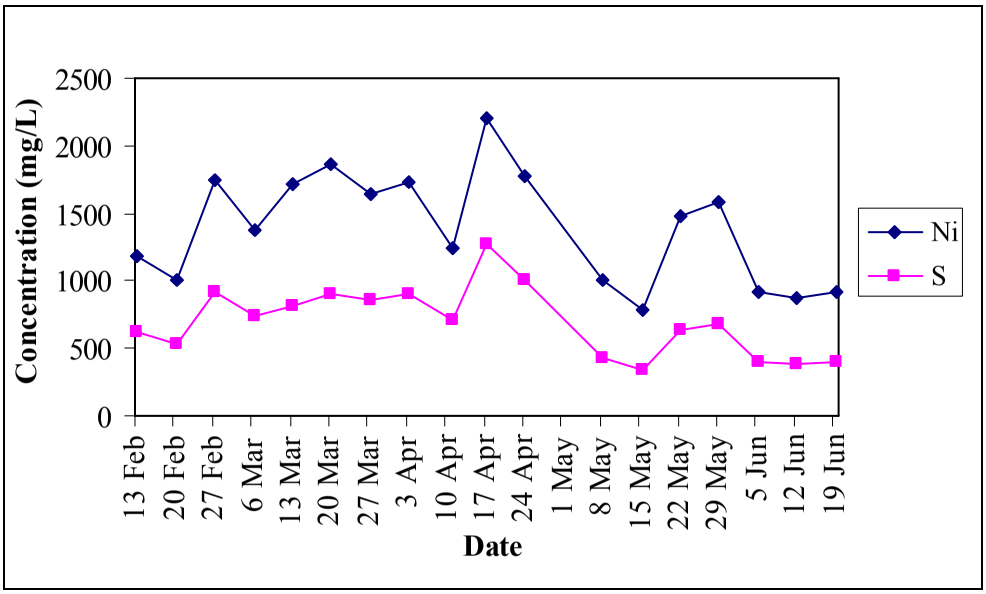

Figure B22 Concentration profile of Tank 20

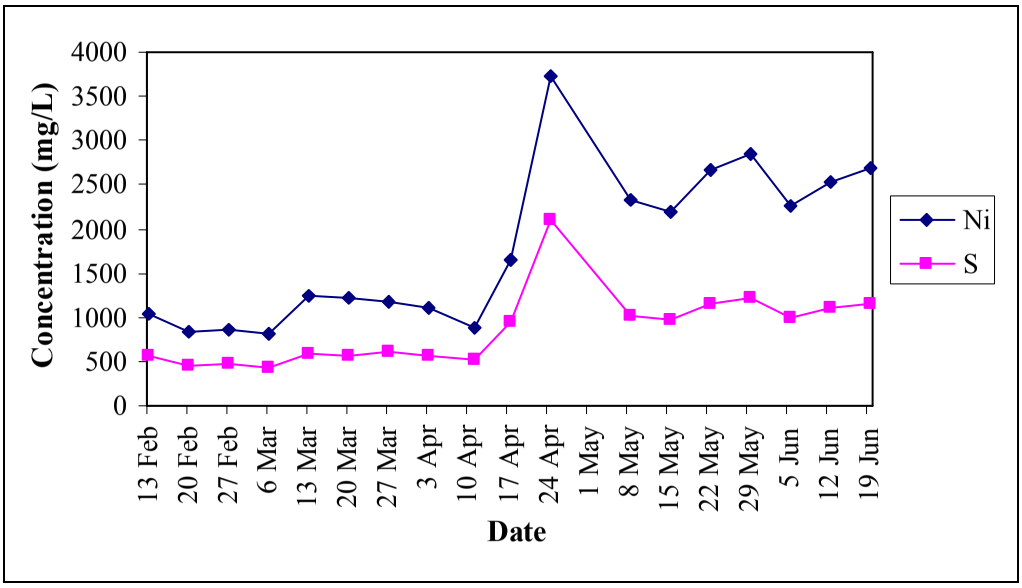

Figure B23 Concentration profile of Tank 21

APPENDIX C

The operating cycles (OC) and sample periods within each operating cycle are given below. These operating cycles were used in Section 8.4 for the drag-out determinations.

Table C1 Operating cycles and sample periods for Tank 2

Operating Cycle (OC)	Sample Period (SP)	Date from the start to end of SP	Number of working days in SP
1	1	13/02 to 19/02	5
2	2	20/02 to 26/02	5
	3	27/02 to 5/03	5
	4	6/03 to 12/03	5
	5	13/03 to 19/03	5
	6	20/03 to 26/03	4
3	7	27/03 to 2/04	5
	8	3/04 to 10/04	3
	9	11/04 to 16/04	5
	10	17/04 to 23/04	5
4	11	24/04 to 8/05	9
	12	9/05 to 14/05	4
5	13	15/05 to 21/05	5
	14	22/05 to 28/05	5
	15	29/05 to 4/06	5
	16	5/06 to 11/06	5
	17	12/06 to 18/06	5

Table C2 Operating cycles and sample periods for Tanks 4

Operating Cycle (OC)	Sample Period (SP)	Date from the start to end of SP	Number of working days in SP
1	1	13/02 to 19/02	5
2	2	20/02 to 26/02	5
	3	27/02 to 5/03	5
	4	6/03 to 12/03	5
	5	13/03 to 19/03	5
	6	20/03 to 26/03	4
3	7	27/03 to 2/04	5
	8	3/04 to 10/04	3
	9	11/04 to 16/04	5
	10	17/04 to 23/04	5
4	11	24/04 to 8/05	9
	12	9/05 to 14/05	4
	13	15/05 to 21/05	5
	14	22/05 to 28/05	5
	15	29/05 to 4/06	5
	16	5/06 to 11/06	5
	17	12/06 to 18/06	5

Table C3 Operating cycles and sample periods for Tanks 8

Operating Cycle (OC)	Sample Period (SP)	Date from the start to end of SP	Number of working days in SP
1	1	13/02 to 19/02	5
	2	20/02 to 26/02	5
	3	27/02 to 5/03	5
	4	6/03 to 12/03	5
	5	13/03 to 19/03	5
	6	20/03 to 26/03	4
2	7	27/03 to 2/04	5
	8	3/04 to 10/04	3
	9	11/04 to 16/04	5
	10	17/04 to 23/04	5
3	11	24/04 to 8/05	9
	12	9/05 to 14/05	4
	13	15/05 to 21/05	5
	14	22/05 to 28/05	5
	15	29/05 to 4/06	5
	16	5/06 to 11/06	5
	17	12/06 to 18/06	5

Table C4 Operating cycles and sample periods for Tanks 12

Operating Cycle (OC)	Sample Period (SP)	Date from the start to end of SP	Number of working days in SP
1	1	13/02 to 19/02	5
	2	20/02 to 26/02	5
	3	27/02 to 5/03	5
2	4	6/03 to 12/03	5
	5	13/03 to 19/03	5
	6	20/03 to 26/03	4
3	7	27/03 to 2/04	5
	8	3/04 to 10/04	3
	9	11/04 to 16/04	5
	10	17/04 to 23/04	5
4	11	24/04 to 8/05	9
	12	9/05 to 14/05	4
	13	15/05 to 21/05	5
	14	22/05 to 28/05	5
	15	29/05 to 4/06	5
	16	5/06 to 11/06	5
	17	12/06 to 18/06	5

Table C5 Operating cycles and sample periods for Tank 18

Operating Cycle (OC)	Sample Period (SP)	Date from the start to end of SP	Number of working days in SP
1	1	13/02 to 19/02	5
	2	20/02 to 26/02	5
	3	27/02 to 5/03	5
2	4	6/03 to 12/03	5
	5	13/03 to 19/03	5
	6	20/03 to 26/03	4
3	7	27/03 to 2/04	5
	8	3/04 to 10/04	3
	9	11/04 to 16/04	5
	10	17/04 to 23/04	5
4	11	24/04 to 8/05	9
	12	9/05 to 14/05	4
	13	15/05 to 21/05	5
	14	22/05 to 28/05	5
	15	29/05 to 4/06	5
	16	5/06 to 11/06	5
	17	12/06 to 18/06	5

APPENDIX D

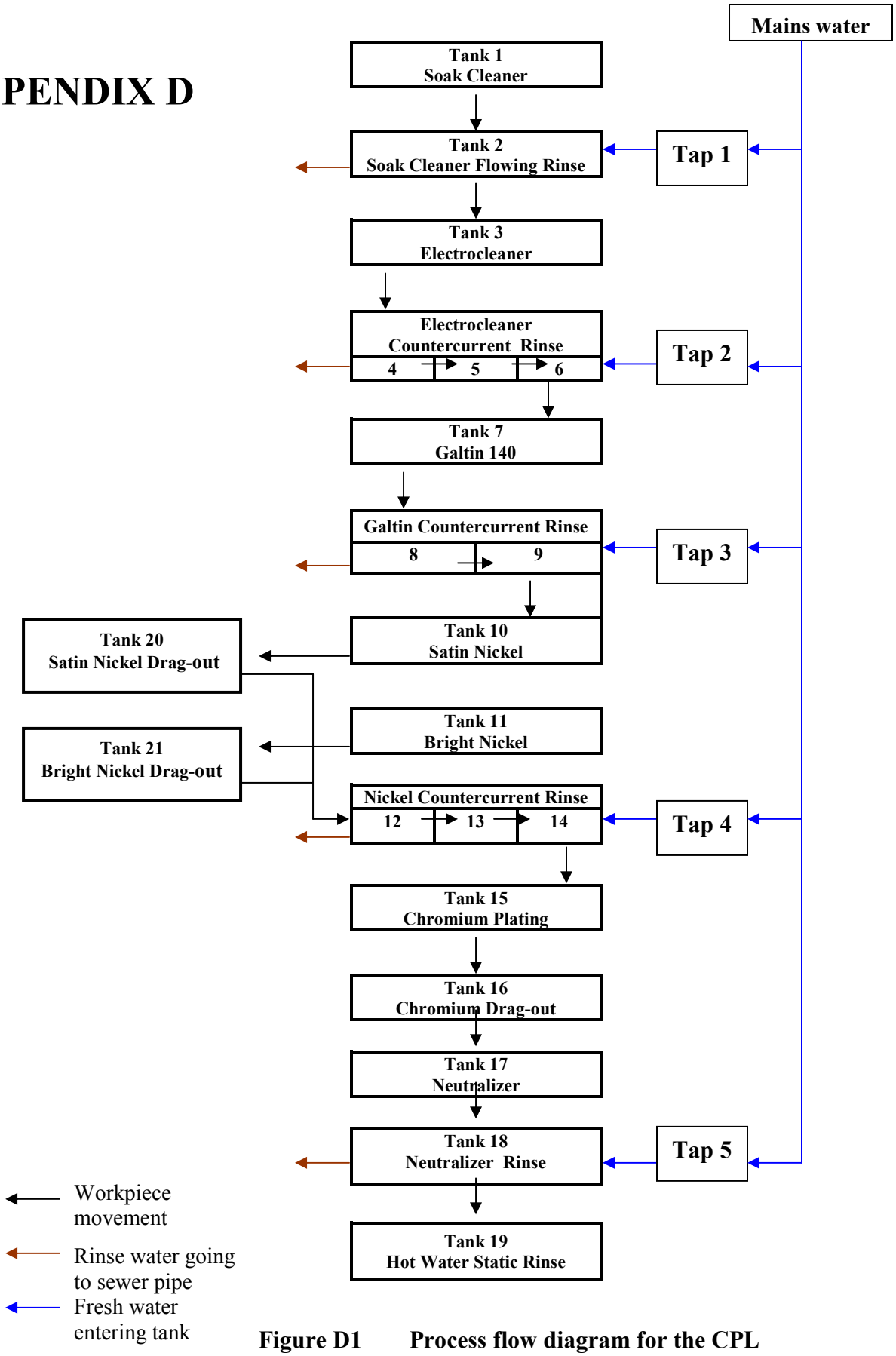

Figure D1 Process flow diagram for the CPL